

Influence of water on the physical properties of fluoride glass

M.C. Gonçalves and R.M. Almeida

Centro de Física Molecular / INESC, Instituto Superior Técnico, Av. Rovisco Pais, 1000 Lisbon, Portugal

A.T. Delben and M.A. Aegerter

Instituto de Física e Química de São Carlos, CEP 13560, São Paulo, Brazil

Several physical properties of ZBLAN glass, including their characteristic transformation temperatures, density, refractive index and ultrasonic velocity, were studied as a function of their residual water content. A series of samples with OH concentrations up to $\sim 0.0043 \text{ mol dm}^{-3}$ was prepared. The OH content was determined for the partially hydrated glasses from FTIR measurements, using a known molar extinction coefficient value for the $2.9 \mu\text{m}$ band, assigned to fundamental OH stretching vibrations in Zr-OH species. Molecular H_2O was not found at the present levels of water concentration. The preliminary results obtained indicate that an increase in the OH concentration causes a decrease of the density and refractive index values, similar to what has been observed in $\nu\text{-SiO}_2$, as opposed to the case of silicate glasses. This behavior was not expected, since ZBLAN glass has a complex structure closer to that of modified silicates than to $\nu\text{-SiO}_2$. The effect of the OH concentration on the other physical properties was generally found to coincide with known trends for silicate glasses.

1. Introduction

Heavy metal fluoride glasses are of technological interest due to their high intrinsic transparency to middle infrared radiation, which makes them good candidates for long haul fiber optics. However, extrinsic absorption and scattering may dramatically increase their optical attenuation, reducing potential applications. While great efforts have been directed toward the preparation of high quality glasses with low attenuation, little work has been performed with the goal of correlating specific impurities with changes in the physical and chemical properties of these glasses.

The main purpose of the present study is to correlate the presence of small concentrations of water on certain physical properties of ZrF_4 -based fluoride glass. The effect of the water content on the physical properties of vitreous silica and modified silicate glasses is relatively well understood [1-6], as opposed to the situation with fluoride glasses. It is well known that a water incorpora-

tion of, for example, 0.01 wt% has a significant effect on certain physical properties of the former glasses [7]. In vitreous silica, an *increase* in water content causes a *decrease* in the density and refractive index. The incorporation of OH groups renders the structure more open, thus increasing the volume [2]. In modified silicate glasses, an increase in water content causes an *increase* in both the density and refractive index. This was explained by the occurrence of hydrogen bonding, which causes shrinkage of the glass network [2]. In both silica and silicate glasses, the presence of water causes the thermal expansion coefficient to increase and T_g to decrease. This was explained as due to an increasing asymmetry of the structure, in addition to its weakening [2].

The ultrasonic velocity is found to decrease as the water content increases, in both silica and silicate glasses [2] which was explained by the lower rigidity of the structure obtained. Mechanical properties such as the elastic moduli behave similarly to the ultrasonic velocities [2].

2. Experimental

All glass samples studied in this work had the same composition (57ZrF₄-28.1BaF₂-3.3LaF₃-5AlF₃-6.6NaF, in mol%) and they are designated by ZBLAN_{6,6}. Starting materials were ZrF₄ (GFI, 99%), LaF₃ (Alfa-Ventron, 99%), anhydrous AlF₃ (Alfa-Ventron, 99.5%), plus BaF₂ and NaF (both Ultrapure, Alfa Products). The reference glass samples were melted in a dry box and they were cast into a preheated graphite mold in the shape of parallelepipeds with approximate dimensions of ~ 20 × 12 × 8 mm. Detailed preparation methods have been described elsewhere [8,9]. The hydrated glasses were prepared according to a similar procedure, but in open air of varying humidities.

The OH content was calculated for the hydrated glasses based on infrared absorption spectroscopy measurements, using a molar extinction coefficient value derived from the literature [10,11] for the 2.9 μm band, assigned to fundamental OH stretching vibrations in Zr-OH species [12,13]. The water concentration, *C*, which was found to correspond exclusively to OH groups, given the absence of a molecular water peak near 6.1 μm [12], was calculated by

$$C = A/\epsilon l, \quad (1)$$

where *A* is the absorbance at the maximum of the 2.9 μm band, ϵ is the molar extinction coefficient and *l* is the sample thickness.

Density values, *d*, were measured at 25 °C by buoyancy in CCl₄, and they were accurate to ±0.001 g cm⁻³. Refractive indices, *n_D*, for the sodium D line (λ = 589.3 nm) were measured with an Abbé refractometer at 25 °C, and they were accurate to within ±0.0002.

Differential scanning calorimetry (DSC) scans were performed on unground chips of glass ~ 4 mg in weight, in a Perkin-Elmer DSC7 calorimeter, with a heating rate of 10 °C/min, between 200 and 600 °C.

Fourier transform infrared (FTIR) spectra were recorded at room temperature, between 7000 and 700 cm⁻¹, in a Nicolet 5DXC spectrometer, equipped with a DTGS detector. An aver-

age of 100 scans were collected at 4 cm⁻¹ resolution.

Ultrasonic measurements were performed by a pulse echo method with a Matec Pulse modulator/receiver model 6600 with quartz transducers. An elastic pulse was generated by the piezoelectric transducer coupled to one of the sample faces, which was reflected on the opposite face and back detected by the same transducer. The pulse transit time, *t*, was measured with a Hewlett-Packard oscilloscope model 1741 A and the ultrasonic velocity, *v* (m/s), was calculated by the equation

$$v = 2L/t, \quad (2)$$

where *L* is the sample length (in meters) and *t* is the pulse transit time (in seconds). According to the transducer used, the longitudinal (*v_l*) or transverse (*v_t*) ultrasonic velocities were obtained.

3. Results

Assuming the validity of the Lambert-Beer law for the OH stretching vibrational peak in the infrared spectrum of fluoride glasses at the present hydration levels, the OH content is directly proportional to the extinction coefficient. Values for this are given in the literature for a series of different fluorozirconate glass compositions [10, 11, 14-17]. Although none of these coincided exactly with the present ZBLAN_{6,6} composition, the ϵ_{OH} value of a ZBLA composition [10] which was closest to ZBLAN_{6,6} was used. This ϵ_{OH} value might affect the calculated OH concentration to some extent.

Figure 1 shows the IR spectra of a reference ZBLAN_{6,6} glass and two hydrated ZBLAN_{6,6} samples in the middle IR transparency region. None of these glasses showed any significant absorption near 1600 cm⁻¹, ruling out the presence of surface or bulk molecular water, at the present levels of water concentration. The OH concentrations were ~ 0.0023-0.0043 mol dm⁻³ for the hydrate samples, and 0.00043 mol dm⁻³ for the reference sample, on the basis of $\epsilon_{\text{OH}} = 13.0$ dm³/mol cm [10]. The density and refractive in-

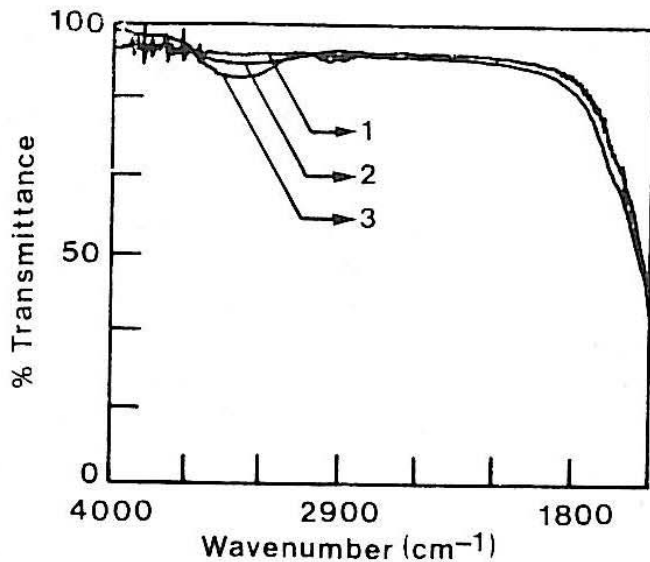


Fig. 1. IR spectra of ZBLAN_{6.6} glasses: 1, reference; 2, hydrated with [OH] = 0.0023 mol dm⁻³; 3, hydrated with [OH] = 0.0043 mol dm⁻³ (thickness = 6.8 mm).

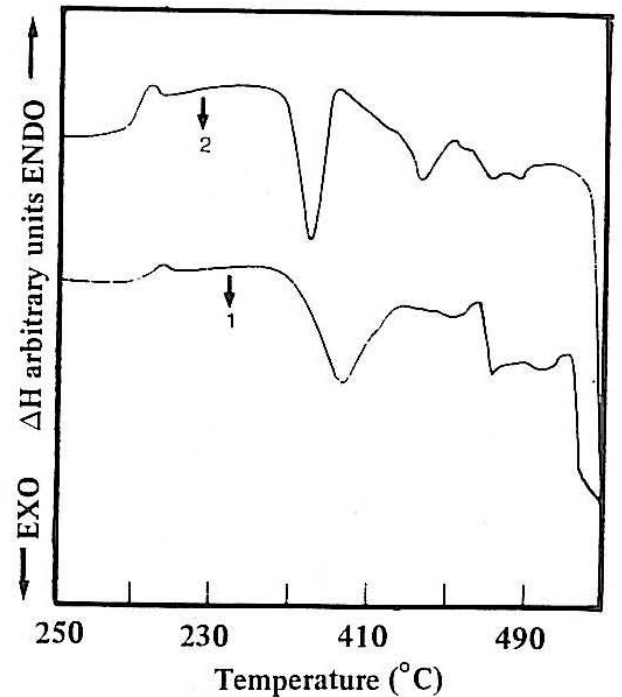


Fig. 2. DSC scans of (1) hydrated ZBLAN_{6.6} with [OH] = 0.0043 mol dm⁻³ and (2) reference ZBLAN_{6.6}.

dex values of the different glass samples are given in table 1. DSC scans, two examples of which are shown in fig. 2, furnished values for the temperatures of glass transition, (T_g), and onset of crystallization, T_c , which are also given in table 1.

The transverse, v_t , and longitudinal, v_l , ultrasonic velocities, Young's modulus, E , shear modulus, G , bulk modulus, K , and Poisson's ratio, ν ,

are given in table 2. The elastic constants were determined through eqs. (3)–(6):

$$E = dv_l^2 \frac{3v_t^2 - 4v_l^2}{v_l^2 - v_t^2}; \quad (3)$$

Table 1
Physical properties of anhydrous and hydrated ZBLAN_{6.6} glasses

	n_D	d (g/cm ³)	T_g (°C)	T_x (°C)	$(T_x - T_g)/T_g$
ZBLAN _{6.6} anhydrous	1.5137	4.530	292.3	374.4	0.1452
ZBLAN _{6.6} hydrated ^{a)}	1.5135	4.501	289.1	377.8	0.1578
ZBLAN _{6.6} hydrated ^{b)}	1.5135	4.502	287.7	365.5	0.1388
ZBLAN _{6.6} hydrated ^{c)}	1.5130	4.507	287.7	365.5	0.1388

^{a)} [OH] = 0.0023 mol dm⁻³.

^{b)} [OH] = 0.0020 mol dm⁻³.

^{c)} [OH] = 0.0043 mol dm⁻³.

Table 2
Mechanical properties of anhydrous and hydrated ZBLAN_{6.6} glasses

	v_t (m/s)	v_l (m/s)	ν	G (GPa)	E (GPa)	K (GPa)
ZBLAN _{6.6} anhydrous	2073.2	3908.0	0.30	19.5	50.8	43.3
ZBLAN _{6.6} hydrated ^{a)}	2117.6	3927.3	0.30	20.3	52.5	42.7
ZBLAN _{6.6} hydrated ^{b)}	2211.4	4029.6	0.29	22.0	56.6	43.8

^{a)} [OH] = 0.0023 mol dm⁻².

^{b)} [OH] = 0.0020 mol dm⁻³.

$$G = dv_t^2; \quad (4)$$

$$K = d \frac{3v_1^2 - 4v_t^2}{3}; \quad (5)$$

$$\nu = \frac{v_1^2 - 2v_t^2}{2(v_1^2 - v_t^2)}. \quad (6)$$

4. Discussion

At the present levels of water concentration, a slight tendency for decreasing density (and refractive index, although this exhibited changes only in the fourth decimal figure) with increasing OH content was noticed, similar to what has been observed in v-SiO₂. This result was unexpected, since ZBLAN glass has a complex structure closer to modified silicates than to v-SiO₂ [18]. Therefore, this indicates that the structure of the glass becomes slightly more open when mildly hydrated, contrary to what one observes in glasses with larger water contents [19]. The reduced parameter $(T_x - T_g)/T_g$ provides a measure of the glass-forming ability, i.e., the resistance to devitrification [8]. There was a tendency for this parameter to decrease with increasing OH content, essentially because of a decrease in T_g , underlining an increasing tendency for crystallization with larger water contents.

At the present hydration levels, the transverse and longitudinal ultrasonic velocities remain essentially constant, within the experimental error estimated at $\pm 3\%$ and the same conclusion follows for the calculated elastic constants. The magnitude of the experimental values was in agreement with previously published data [20].

5. Conclusions

A series of ZBLAN glass samples was studied with different OH concentrations between 0.0023 and 0.0043 mol dm⁻³. At these intermediate levels of hydration, which were low compared with previous studies of silicate glasses, but were large compared with the residual levels present in optical fiber quality fluorozirconate glasses, the den-

sity, refractive index and characteristic temperatures appeared to decrease with the OH content. This behavior was different from that of modified silicate glasses, with respect to the density and refractive index changes, suggesting that the extent of hydrogen bonding in the present glasses might be the dominant factor. This aspect is currently being investigated in greater detail [19].

Two of the authors (M.C.G. and R.M.A.) wish to acknowledge the financial support of INIC and also that of JNICT and CNPq, through a Luso-Brazilian cooperation agreement for scientific exchange. A.T.D. and M.A.A. would also like to thank Professor J.A. Eiras of UFSCar, for making available the equipment for ultrasonic measurements and for his kind assistance during the above.

References

- [1] G. Hetherington and K.H. Jack, *Phys. Chem. Glasses* 3 (1962) 129.
- [2] E.N. Boulou and N.J. Kreidl, *J. Can. Ceram. Soc.* 41 (1972) 83.
- [3] R.F. Bartholomew, B.L. Butler, H.L. Hoover and C.K. Wu, *J. Am. Ceram. Soc.* 63 (1980) 481.
- [4] J.E. Shelby, J. Vitko Jr. and R.E. Benner, *J. Am. Ceram. Soc.* 65 (1982) C-59.
- [5] R.F. Bartholomew and J.W.H. Schreurs, *J. Non-Cryst. Solids* 38&39 (1980) 679.
- [6] R.F. Bartholomew, *J. Non-Cryst. Solids* 56 (1983) 331.
- [7] J.P. Williams, J.S. Su, W.R. Strzegowski, B.L. Butler, H.L. Hoover and V.O. Altemose, *J. Am. Ceram. Soc. Bull.* 55 (1976) 5.
- [8] J.L. Grilo, M.C. Gonçalves and R.M. Almeida, *Mater. Sci. Forum* 19&20 (1987) 299.
- [9] M.C. Gonçalves, J.C. Pereira and R.M. Almeida, *Mater. Sci. Forum*, in press.
- [10] S. Mitachi, G. Fonteneau, P.S. Christensen and J. Lucas, *J. Non-Cryst. Solids* 92 (1987) 313.
- [11] S. Mitachi, G. Fonteneau, P.S. Christensen and J. Lucas, *J. Non-Cryst. Solids* 92 (1987) 326.
- [12] R.M. Almeida, M.C. Gonçalves and J.L. Grilo, *Mater. Sci. Forum* 32&33 (1988) 427.
- [13] M. Robinson, K.C. Fuller and R.C. Pastor, *J. Non-Cryst. Solids* 110 (1989) 279.
- [14] S. Mitachi, S. Sakaguchi and S. Takahashi, *Phys. Chem. Glasses* 27 (1986) 144.
- [15] G. Fonteneau, D. Trégoat and J. Lucas, *Mater. Res. Bull.* 20 (1985) 1047.

- [16] P.S. Christensen, G. Fonteneau, J. Lucas and S. Mitachi, *Mater. Sci. Forum* 19&20 (1987) 203.
- [17] D. Trégoat, G. Fonteneau, J. Lucas and C.T. Moynihan, *Mater. Sci. Forum* 5 (1985) 323.
- [18] See, for example, R.M. Almeida, in: *Halide Glasses for Infrared Fiberoptics*, éd. R.M. Almeida (Nijhoff, Dordrecht, 1987) p. 57.
- [19] M.C. Gonçalves and R.M. Almeida, to be published.
- [20] M.P. Brassington, T. Hailing, A.J. Miller and G.A. Saunders, *Mater. Res. Bull.* 16 (1981) 613.