Journal of Non-Crystalline Solids 161 (1993) 165–168
North-Holland

JOURNAL OF
NON-CRYSTALLINE SOLIDS

Mechanical properties of ZBLAN glasses

A. Delben, Y. Messaddeq, M.D. Caridade and M.A. Aegerter
Universidade de São Paulo, Cx. Postal 369, 13560–250 São Carlos (SP), Brazil

J.A. Eiras
Universidade Federal de São Carlos, 13565–905 São Carlos (SP), Brazil

Elastic moduli (E, G, K, ν) of various ZBLAN glass compositions have been determined using pulse echo ultrasonic technique. Vickers microhardness, H_v, was measured under 100 g load and also determined systematically as a function of the load (30–125 g) for a $ZBLAN_{11.6}$ composition submitted to different surface treatments such as storage in dry and wet atmosphere and optical polishing. In all cases, H_v increases with load until reaching an almost constant value $H_v \simeq 200$ kg/mm^2 for load >100 g. The hardness variation with load is similar for as-prepared glasses stored in dry or wet atmosphere but is more pronounced for samples with a polished surface. The results are explained by a model which assumes that H_v is determined by the weighted average of plastically deformed volumes in a surface layer and in the bulk. The model allows one to estimate their microhardness and the thickness of the surface layer.

1. Introduction

Elastic moduli in fluoride glasses have been usually determined indirectly from the velocity of sound in the glass. ZBLAN compositions are among the most stable fluoride compositions and have a Young's modulus near 55–60 GPa, a shear modulus around 20 GPa and a Poisson's ratio between 0.25 and 0.30. Slightly higher values are observed for glass composition having higher T_g. For $(1-x)$ZBA–xRF, where RF is a single alkali or mixed species, Zhao and co-workers [1,2] found that the Young's modulus fell by up to 25% as the alkali level increases from 0 to 20%, an effect especially marked with KF and least with LiF. The microhardness of these glasses is around 2.2 GPa, about half of those for silicates, consistent with the reduced bond lengths. The values are also higher for glasses having higher T_g. These glasses are used for fiber drawing and it is expected that their Young's modulus will be lower than bulk glass specimens because of their more open structure quenched in during the fabrication. In this paper we present a study of the elastic properties of a series of ZBLAN glasses of compositions (mol%) $57ZrF_4$–$(28.1-x)BaF_2$–$3.3LaF_3$–$5AlF_3$–$(6.6+x)NaF$ as a function of NaF content ($0 \le x \le 13.4$) and a systematic study of the Vickers hardness of $ZBLAN_{11.6}$ as a function of load and surface treatments. The latter results are analyzed with a model involving weighted average of plastically deformed volumes near the surface and in the bulk, allowing the determination of their true microhardness and the thickness of the surface layer.

Correspondence to: Professor Dr M.A. Aegerter, Instituto de Fisica e Quimica de São Carlos, Universidade de São Paulo, Cx. Postal 369, 13560–250 São Carlos (SP), Brazil. Tel: +55-162 749 206. Telefax: +55-162 713 616.

2. Experiment

Glasses have been fabricated in a glove box under dry Ar atmosphere by conventional melting and quenched in metallic mold. The elastic constants such as Young's modulus, E, shear modulus, G, bulk modulus, K, and Poisson's ratio, ν, have been determined through eqs. (1)–(4), respectively, where v_l and v_t are the longitudinal and transversal ultrasonic velocities determined by a pulse echo method previously described [3] and ρ is the glass density:

$$E = \rho v_t^2 \frac{3v_l^2 - 4v_t^2}{v_l^2 - v_t^2}; \quad (1)$$

$$G = \rho v_t^2; \quad (2)$$

$$K = \rho(3v_l^2 - 4v_t^2)/3; \quad (3)$$

$$\nu = \frac{v_l^2 - 2v_t^2}{2(v_l^2 - v_t^2)}. \quad (4)$$

Vickers microhardness was determined with a Carl Zeiss 160 Microhardness Tester by measuring the diagonals of at least 10 indentations for each load and calculated in kg/mm^2 by

$$H_v = 1854.4(P/d^2) \quad (5)$$

where P (g) is the load and d (μm) is the diagonal length average of the indent. Measurements were performed by the same operator. The determination of the role of humidity and polishing required three series of sample.

(i) Series A: glasses prepared in a dry box by pouring the melt in mould with parallel faces. The samples were kept in the dry box and measured under dry atmosphere.

(ii) Series B: the same samples were then stored in ambient atmosphere (relative humidity ~ 50%) for a couple of days; measurements were then performed in air.

(iii) Series C: samples of the series B were optically polished down to 0.25 μm and H_v determined.

The detailed procedure is described elsewhere [3]. The load range was varied between 30 and 125 g and was limited by visual difficulties under 30 g and crack occurrence beyond 125 g.

3. Results

The elastic constants, the average velocities and the microhardness measured with a 100 g load are given in table 1 for seven ZBLAN glasses with different NaF concentration. G and H_v slightly increase with the substitution of BaF_2 by NaF while K fluctuates and ν varies between 0.27 and 0.31.

Figure 1 shows the load variation of the microhardness for the three series of $ZBLAN_{11.6}$ glass. The first two series show a surprising matching indicating that humidity, the only parameter which was different for these samples, does not affect severely the microhardness. For both series, H_v increases with load up to 110 g and then levels off for heavier loads. In the third series, microhardness also increases with load and approaches the previous results at high load; the values are smaller than the previous ones for $P \leq 90$ g. The load influence is therefore more pronounced for polished surfaces, but, at high loads, H_v is practically identical for the three series.

Meyer's empirical rule [4] related the applied load, P, to the length of the diagonal as $P = kd^i$ where k is a constant characteristic of the material and i is the 'Meyer index'. H_v does not depend on the load if $i = 2$. The values of the Meyer index are given in table 2. Their values are

Table 1
Elastic constants E, G, K, ν, average sound speed, v_m, and microhardness, H_v, of various $ZBLAN_x$ glasses

NaF (%)	E (GPa) (±2 GPa)	G (GPa) (±1 GPa)	K (GPa) (±3 GPa)	ν	v_m (m/s) (±60 m/s)	H_v (kg/mm²) (±10 kg/mm²)
7.6	53.3	20.5	44.2	0.299	2400	–
8.6	51.2	19.9	40.0	0.286	2361	213
9.6	53.7	20.7	43.6	0.290	2420	195
10.6	54.2	21.8	46.5	0.310	2430	208
11.6	54.3	21.0	43.3	0.290	2443	180
16.6	55.0	21.7	39.1	0.270	2413	198
20.0	55.0	21.3	43.8	0.290	2497	220

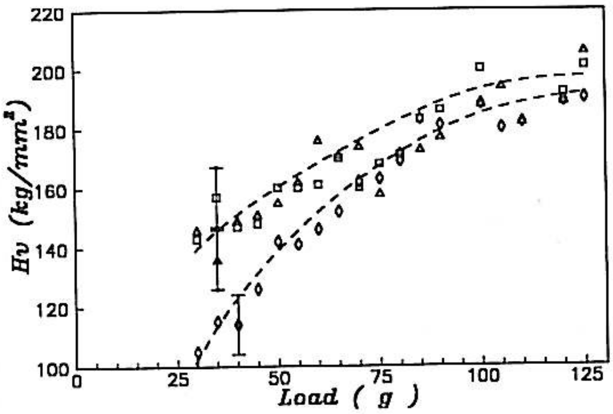

Fig. 1. Microhardness versus load for $ZBLAN_{11.6}$ glass. △, series A; □, series B; ◇, series C.

almost constant and are slightly over the value $i = 2$ for the first two series and series C at high load but the series C value increases to 3.9 at low load. These results suggest that, since polishing is a standard procedure before microhardness measurements, such determination should be done under loads larger than 100 g.

4. Discussion

Fabes et al. [5] proposed a model to explain thin film hardness based on the contributions of coating and substrate weighted by the volumes affected by the indenter. We use the same model making an analogy between the film and a perturbed polished surface and the substrate and the bulk of the sample.

This model takes into account the influence of a plastically deformed volume that reaches the bulk before the indenter as the indentation depth increases. In order to simplify the calculations, the deformed volume is approximated by a 45° triangular cone as shown in fig. 2. The indentation sequence is divided in three stages.

Table 2
Meyer index, i, of $ZBLAN_{11.6}$ glass

Series	Load range (g)	i
A	30– 80	2.34
	90–125	2.22
B	30– 80	2.48
	90–125	2.49
C	30– 80	3.87
	80–125	2.46

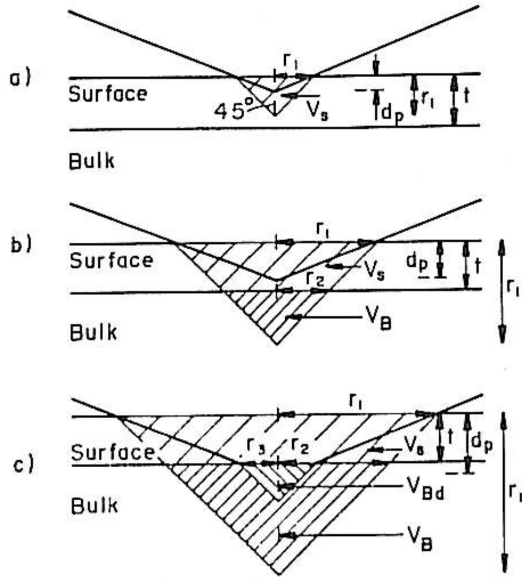

Fig. 2. Indentation and characteristic dimension in each stage (from ref. [5]).

(a) In the first stage, both indenter and its associated plastic strain field are confined within the surface layer and the hardness is that of the surface and independent of the depth (fig. 2(a)):

$$H^{\mathrm{I}} = H_{\mathrm{s}}. \tag{6}$$

(b) In the second stage, the indenter is still in the surface layer, but the associated plastic strain field has penetrated into the bulk. The hardness is given by eq. (7), where α ranges from 1 to 1.5, E_{S} and E_{V} are the Young's moduli of the surface layer and the bulk respectively and V_{S} and V_{B} are the deformed volumes (fig. 2(b)):

$$H^{\mathrm{II}} = \frac{H_{\mathrm{s}} V_{\mathrm{s}} \left(\dfrac{E_{\mathrm{s}}}{E_{\mathrm{B}}} \dfrac{H_{\mathrm{B}}}{H_{\mathrm{s}}} \right)^{\alpha} + H_{\mathrm{B}} V_{\mathrm{B}}}{V_{\mathrm{s}} \left(\dfrac{E_{\mathrm{S}}}{H_{\mathrm{S}}} \dfrac{H_{\mathrm{B}}}{E_{\mathrm{B}}} \right)^{\alpha} + V_{\mathrm{B}}}. \tag{7}$$

(c) In the third stage the indenter itself has penetrated into the bulk (fig. 2(c)). There is an additional contribution to the bulk strain volume from material which is deformed directly by the indenter. This volume, V_{Bd}, is

$$V_{\mathrm{Bd}} = \frac{\pi}{3}(0.57) r_1^3 \tag{8}$$

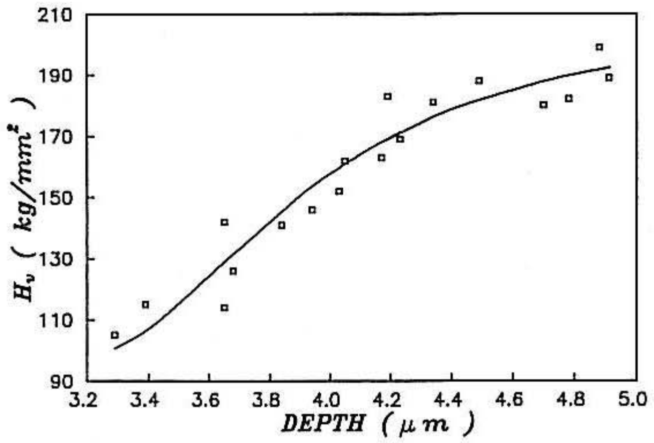

Fig. 3. Microhardness versus depth of $ZBLAN_{11.6}$ glass with the theoretical fit.

and the microhardness is given by

$$H^{\mathrm{III}} = \frac{H_S V_S \left(\frac{E_S}{H_S} \frac{H_B}{E_B} \right)^{\alpha} + H_B V_B + H_B V_{Bd}}{V_S \left(\frac{E_S}{H_S} \frac{H_B}{E_B} \right)^{\alpha} + V_B + V_{Bd}}. \quad (9)$$

In our experiment we do not reach the low load values where microhardness is constant (first stage); at 30 g we are already in the second stage and the maximum depth of the indenter is 5 μm. The fit of eq. (7) to the data is shown in fig. 3 with the following values of the parameters: surface layer thickness, $t = 10.5$ μm; surface microhardness, $H_S = 95$ kg/mm^2; $\alpha = 1.3$; bulk microhardness, $H_B = 215$ kg/mm^2; and $(E_S/E_B)^{\alpha} = 0.005$ and since $E_B = 54.3$ GPa, then $E_S = 0.92$ GPa. The values of H_v measured under the highest load appear therefore slightly smaller than the model value of the bulk hardness.

5. Conclusions

Elastic moduli (E, G, K, ν) of several ZBLAN glass compositions have been determined as a function of their NaF content. The microhardness of $ZBLAN_{11.6}$ has been measured after various surface treatments. In all cases, H_v increases with the load and levels at $H \sim 200$ kg/mm^2 for load ≥ 120 g. The data are in agreement with a model in which the microhardness is due to contributions of an external layer of thickness ~ 10 μm and $H_S \sim 95$ kg/mm^2 and a bulk with $H_B \sim 215$ kg/mm^2 weighted by volumes plastically deformed by the indenter. The thickness and microhardness of the surface layer are affected by the polishing process.

This research was sponsored by FAPESP, TELEBRAS, CNPq, CAPES and RHAE-NM (Brazil). A.D. thanks J.R. Delben for helping in the calculations.

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