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Influence of water adsorption on mechanical properties of porous glasses

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An influence of different treatment of porous glass (water adsorption, heat or hexamethyldisilazane treatment) on the values of elasticity parameters was investigated. The laboratory ultrasonic tests were used to determine the dynamical elastic modulus. The observed changes of the dynamic elastic modulus of porous glasses were related with processes of adsorption and desorption of water from the pores.

1. Introduction

Silica porous glasses – the products of etching of phase separated alkali borosilicate glasses – are widely used as optical recording media and gradient refractive index devices [1]–[3]. They contain a net of interconnected pores. In the case where the dimensions of these devices change under external conditions, distortion of the recorded information may occur. While thermal extension of porous glasses consisting of almost pure silica is very small, significant mechanical stresses and corresponding extensions arise when these materials are placed in a humid atmosphere. For application of porous glasses it is very important to minimize these stresses.

The ultrasonic tests are a non-destructive technique for determining elastic properties of different materials [4]. In this paper, this technique was applied to calculation of the dynamic elastic modulus of porous glasses. We have performed investigation of the mechanical properties of porous glasses. The influence of different treatment of glasses on their elasticity parameters was determined. There are some possibilities of removing water from the pores. This can be done, in particular, by heating or a special treatment of the surface-active chemical agent.

2. Experiment

The measurements of elastic properties were made for three types of porous glasses (E, G and H). These glasses were produced from the sodium borosilicate glass [5], [6]. The glasses were heated at different temperatures and for different times – glass E0 was held at 490 °C for 165 h, glass G0 at 650 °C for 100 h. During heating the phase separation into two interconnected and continuous phases occurred. Glasses E and G were obtained from glasses E0 and G0, respectively, after leaching in HCl solution. Glass H was fabricated from glass G after additional treating in KOH. The porosity of the glasses (measured as decrement of mass after technological procedure) amounted to: 37% for glass E, 34% for glass G, and 47% for glass H. The dimensions of all the glass samples amounted to $30 \times 30 \times 0.5$ mm^3. For measuring the elastic properties of E0 and G0 the glass samples had the shape of a cylinder of 36 mm in diameter and 30 mm in height.

The ultrasonic tests were performed with the equipment consisting of UMT-12 supersonic flaw detector, the Ultramet software and two transducers (transmitter and receiver) of 2 MHz frequency. Details concerning the measuring procedures are described in [4]. Dynamical elastic modulus E_d was determined from the measurements of longitudinal V_L, transversal V_T and surface V_S ultrasonic wave velocities. Based on the results of ultrasonic measurements, elasticity parameters of the initial and porous glasses were calculated according to formula (2)

$$\nu = \frac{0.5 - \left(\frac{V_T}{V_L}\right)^2}{1 - \left(\frac{V_T}{V_L}\right)^2}, \tag{1}$$

$$E_d = (V_L)^2 \rho \frac{(1+\nu)(1-2\nu)}{(1-\nu)} \tag{2}$$

where: ν – Poisson ratio, E_d – dynamic elastic modulus, ρ – density.

The dynamic elastic moduli for porous glasses were calculated indirectly using the results of the tests of initial glasses [4]. The elasticity parameters were determined for porous glass before and after:

i) water adsorption (the porous glass sample was kept in water vapour for 10 min. and then heated at 180 °C),

ii) heating of glasses at different temperatures (650 °C, 700 °C and 750 °C, for 30 min.),

iii) treatment in hexamethyldisilazane (HMDS).

3. Results and discussion

The results of measurements of the dynamic elastic modulus for the initial and porous glasses are presented in Tab. 1.

Table 1. Values of dynamic elastic modulus E_d for the glasses under investigatation.

Glass	E0	E	G0	G	H
E_d [10^4 MPa]	4.48–4.63	0.51–1.19	4.51–4.64	1.91–2.00	1.93–2.13

It is evident that the values of the dynamic elastic modulus of porous glasses are lower than values obtained for corresponding initial glasses. It was also found that the value of E_d for the glass G is less than that for the glass H.

When the porous glass is placed in a humid atmosphere, significant mechanical stresses arise. This fact is connected with the change of values of the dynamic elastic modulus after water adsorption of porous glass. The results of these experiments are presented in Tab. 2. The values of the dynamic elastic modulus after water adsorption are lower than initial ones and they increase after heating.

Table 2. The values of the dynamic elastic modulus for porous glasses after water adsorption and heating at 180 °C.

Glass E_d [10^4 MPa]	E	G	H
Before treatment	0.59	1.97	2.12
Water adsorption	0.51	1.72	1.82
After heating	0.61	2.0	2.11

In Table 3, the changes of the dynamic elastic modulus after treatment of the porous glasses in hexamethyldisilazane are shown. An increase of the dynamic elastic modulus is observed.

Table 3. The values of E_d after treatment of porous glasses in HMDS.

Glass E_d [10^4 MPa]	E	G	H
Before treatment	1.19	1.97	1.94
After HMDS	1.22	2.06	1.96

The influence of the heat treatment of the glasses investigated on the values of elasticity parameters is presented in Tab. 4. After heating a significant increase in the dynamic elastic modulus only for glass E is observed. The values of E_d obtained after heating the glasses G and H increase insignificantly and are similar to the values for the unheated glass samples.

The changes of elastic parameters after different treatment are connected with the water adsorbed in the porous glasses. These changes were found to be related with the structure of the porous glass. The E and G glasses are microporous with secondary silica gel inside the pores. Our previous experiments indicate the existence of gel residuals in the pores of the glass H [7]. Depending on water contents, stresses

Table 4. The values of E_d after heat treatment of porous glasses.

Glass E_d [10^4 MPa]	E	G	H
Before treatment	1.10	2.04	2.08
650 °C	2.38	2.07	2.11
700 °C	3.30	2.22	2.13
750 °C	4.14	2.32	2.39

in the glass can be stretching (gel expansion) afterwards compressing (capillary effects) [7]. If the glass is compressed it is more rigid and the dynamic elastic modulus is higher. If the porous glass is kept in water vapour it elongates and is now less rigid, the dynamic elastic modulus is lower. So, a decrease in the value of the dynamic elastic modulus was observed after water adsorption of porous glass (Tab. 2). During heating the porous glass looses water, becomes more rigid and the dynamic elastic modulus increases (Tab. 2). Similar situation is observed after treatment of porous glasses in hexamethyldisilazane (Tab. 3). It is known that HMDS can effectively reduce the number of surface silanol groups substituting them by unpolar methyl groups. Therefore, the physisorption of water molecules becomes impossible and the values of dynamic elastic modulus increase. The increase of the dynamic elastic modulus after heating at high temperature (Tab. 4) can be due to the starting process of the consolidation of pores.

4. Conclusions

Investigations of the dynamic elastic modulus of porous glasses indicate that existence of the silica gel inside the pores deteriorates their mechanical endurance. Additional treatment in hexamethyldisilazane or heating makes porous glass more rigid and the values of the dynamic elastic modulus increase.

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References

[1] NOVIKOV A.F., Glass Physics and Chemistry, Russia, **21** (1995), 58.
[2] KLIM O.V., MESHKOVSKY I.K., Opt. Electron. **83** (1997), 1041.
[3] ALEXEEV-POPOV A.V., ROIZIN YA.O., RYSIAKIEWICZ-PASEK E., MARCZUK K., Opt. Materials **2** (1993), 249.
[4] ŁUKASZEWSKI P., BOGDAŃSKA J., RYSIAKIEWICZ-PASEK E., MARCZUK K., Ceramics **57** (1998), 51.
[5] MAZURIN O.V., PORAI-KOSHITS E., *Phase Separation in Glass*, North-Holland, Amsterdam 1984.
[6] JANOWSKI F., HEYER W., *Porose Glasser*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1981.
[7] GEVELYUK S.A., DOYCHO I.K., RYSIAKIEWICZ-PASEK E., MARCZUK K., J. Porous Materials **7** (2000), 465..

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