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Humidity dependencies of porous sol-gel and silica glass linear sizes*

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Measurements of the porous sol-gel and porous silica glass linear size dependencies on humidity of the surrounding atmosphere were performed using the interferometric techniques. The secondary silica gel existing in the voids of silica porous glasses is absent in the sol-gel glasses. The pore size distributions have two peaks for the sol-gel glass while there are several peaks with decreasing amplitudes in the silica porous glass. The differences in the linear sizes moisture sensitivity are explained by the structure of both types of porous materials. The capillary effects prevail in the last ones. The revealed peculiarities of sol-gel glasses make it possible to develop threshold humidity sensors of a new type.

Key words: *porous glasses, adsorption, desorption, humidity sensor*

1. Introduction

Porous sol-gel glasses are promising materials for a broad spectrum of possible applications in electronics, sensor techniques, pharmacology, prosthetic appliances, etc. The structure and chemical composition of porous sol-gel glasses are close to silica porous glasses [1]. This allows us to investigate them by the techniques developed for silica porous glasses [1–4]. One of these techniques is the carbon treatment. It is based on thermal annealing (450–600 °C) of the porous material with carbon preliminary impregnated into the pores [1, 3]. Reduction of silicon occurs inside the voids due to different chemical activity of both elements and silicon clusters are created in the silica porous glass. These clusters make their contribution to luminescence. The position of spectral maximum is related to the average size of the clusters. These sizes depend,

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first of all, on the sizes of voids in the starting material. Thus, a certain correlation exists between the pore-size distribution and the photoluminescence spectra. Comparison of photoluminescence spectra for silica porous glasses and sol-gel glasses shows that they are practically indistinguishable before carbon treatment [1]. At the same time the positions of light emission peaks differ after this treatment. In the present work, the ambience humidity dependencies of the linear size relative change are compared for porous silica glasses and porous sol-gel glasses.

2. Experimental section

Porous silica glasses were obtained from two-phase alkali borosilicate glasses by alkali borate phase chemical etching. The corresponding technique is discussed in references [5–7]. Porous sol-gel glasses were obtained as described previously [1] from tetraethoxisilane water solution with the ratio of 1 to 4 molar percent. Hydrochloric acid (HC1) with concentration approximately in the range from 30 up to 70% was used as a catalyst in this process. The mixture was stirred at room temperature for about an hour and then was polymerized in polyethylene containers for 100 hours. The obtained samples were dried up in a chamber where the temperature was slowly increased to 600 °C. Both types of the investigated glasses had initial sizes of $10\times15\times0.5$ mm^3.

The humidity dependence of the linear sizes was investigated using the set up based on the Michelson interferometer. One of the interferometer shoulder mirrors was in direct contact with the sample placed in a special gas chamber. The mixture of dry and wet air passed through it. Using the special regulated gas valve system, the humidity of the atmosphere in the chamber could be changed in the range from 10 to 90%. In order to maintain high accuracy of the measurements, the minimal possible rate of gas flow was maintained and the temperature was kept constant. Each subsequent change of humidity was made after complete stabilization of the sample parameters. These parameters were controlled by the position of the fringe pattern movement with respect to the photodiode slot. The 632.8 nm He-Ne laser was used as a light source. The accuracy of 0.001% was achieved in the interferometric measurements of the standard samples with the length of 15 mm. The pore size distribution spectra were obtained by the capacitance method using water vapour absorption-desorption [8, 9].

3. Results and discussion

Figure 1 shows pore size distribution spectra for both porous sol-gel and porous silica glasses. It is necessary to mention that both spectra have similar shape but the distribution is rather mono-disperse (only two fractions) in the first spectrum, while in the second one, case there is a set of peaks with fading amplitude. The number of pores with larger sizes increases. The amount of fractions depends on the properties of the initial glass and on the etching conditions. In the range of pore radii from 0 up to 60 nm four fractions are clearly seen in Fig. 1. However, there were only two peaks in the samples studied in our previous paper [4]. Nevertheless, the void sizes corresponding to these fractions were always larger than in the case of sol-gel glasses.

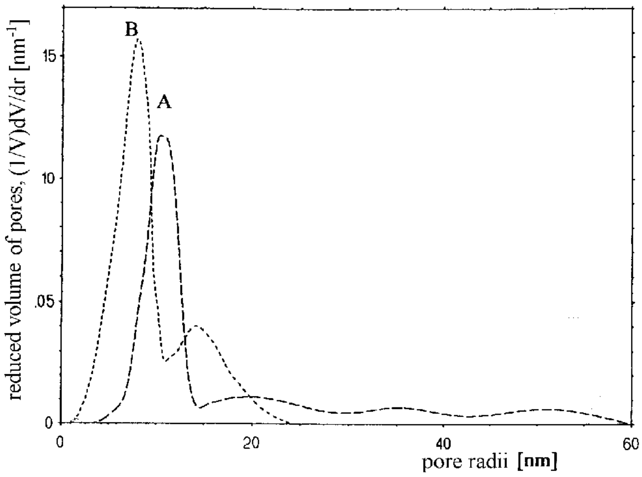

Fig. 1. Size distribution of pores for the silica porous glass (A) and the sol-gel glasses (B)

Microporosity (the average pore size about 2 nm [10]) and almost complete absence of chemical pollution are typical of sol-gel glasses. This is due to the mechanism of their fabrication [11]. The silica porous glasses chosen for comparison with sol-gel specimens were also microporous and the residual silica gel, which was located on the internal pore surface, was almost completely removed by additional chemical treatment in KOH. It is known [6] that certain dissolution of the main framework of silica glass happens as a result of such treatment besides of the secondary silica gel removal. The average pore radius has increased after corresponding over-etch of the pore walls. We want to stress that the traces of secondary silica gel remain after the chemical treatment (as shown in Ref. [4]). Manufacturing of porous glass by the sol-gel technologies gives an opportunity to adjust the pore size and simultaneously excludes the availability of such formation. This explains, in our opinion, different dependencies of linear sizes on humidity for both materials, as shown in Figs. 2 and 3.

The monotonous character of the humidity dependence of the linear sizes for porous silica glass (presented in Fig. 2) in the whole humidity range corresponds to the dominance of the stretching forces connected to swelling of the residual silica gel over the capillary forces of compression. In the case of sol-gel glasses, the character of specified dependencies is essentially different (Fig. 3). Absence of pronounced changes in the specimen size due to in the humidity range from 10% up to 70% suggests that there is no appreciable modification of the pore surface in this range. An abrupt compression of the sample (reaching maximum at 80% humidity) can be explained by the formation of water menisci in the necks of pores with minimum sizes. When humidity is further increased, small voids are filled with water and the moisture begins to be condensed on walls of the pores with greater sizes. It results in almost complete disappearance of the capillary forces (the menisci in these pores is not formed yet) and the size of the sample returns to its initial value. In the case of larger values of humidity the water menisci are created in the fraction of voids with large dimensions (fraction of the diameter 15–17 nm in Fig. 1). The decrease of the sample length in this case is much smaller. This is due to, first, the large radius of the meniscus and, second, the smaller number of corresponding pores. After all the pores are filled with water, the sample length again returns to its initial value.

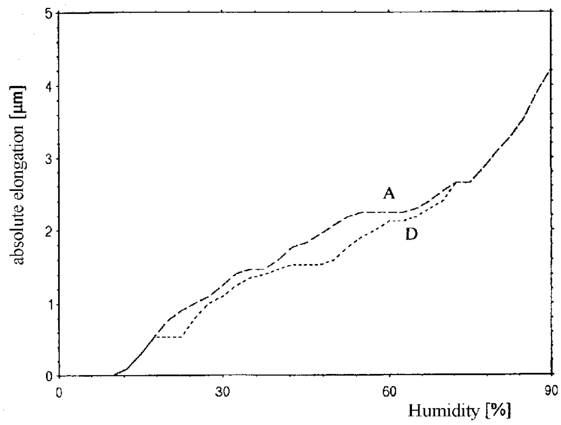

Fig. 2. Dependence of the linear sizes of porous glass during adsorption (A) and desorption (D) on humidity

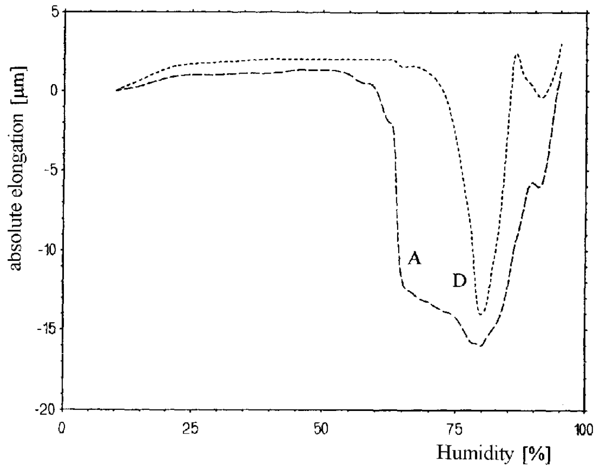

Fig. 3. Dependence of the linear sizes of porous sol-gel glass during adsorption (A) and desorption (D) on humidity

Let us also note that the humidity dependence of the linear size change is more pronounced for the sol-gel glasses in comparison with the similar dependence for the silica porous glasses. We argue that this fact is due to the influence of capillary compression forces only, while no substance similar to the secondary silica gel exists inside the sol-gel glass. No etching was employed in the fabrication process of these glasses and pore formation is the consequence of the glomerular macromolecule structure.

We want to emphasize that the ranges of practical insensitivity to environment humidity for porous sol-gel glasses depend on the pore size distribution. Insensitivity range is wide enough (in Fig. 3 it is about 70%). Adjustment of the specified distribution is possible during the fabrication of porous sol-gel glasses [11]. Thus, it appears possible to create threshold humidity sensors that switch at given humidity and may be used, for example, at the agricultural enterprises and in food industry.

4. Conclusion

Comparison of humidity dependencies of the linear sizes for silica porous glasses and sol-gel glasses has shown that in the latter case the dependence is more pronounced. At the same time there are wide enough areas of insensitivity to humidity. The specified distinctions can be explained by different mechanism of pore formation in both materials. This results in the trade off between residual silica gel swelling (stretching forces) and capillary effects (compressive forces). Besides it, a lot of dangling bonds are created during etching at the internal surface of silica porous glasses that further act as absorption centers for water. The pore surface in sol-gel glasses is more chemically steady. It is possible to regulate the sensitivity threshold in sol-gel glasses and thus to fabricate sensors that switch at given humidity.

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