Estimation of optical heterogeneity of samples in the process of developing nanoporous matrices from two-phase glass

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Abstract. In this paper the research of optical heterogeneity of nanoporous silicate matrices (NPM) by method of digital holographic interferometry (DHI) is presented.

1. Introduction
Currently, the increase of complexity of devices and expanding of the area of application of optical range radiation sets new requirements to optical materials. One of the main ways of development is the creation of new materials with specified properties. Matrix principle of construction of composite materials is one of the prospective.
Nanoporous silicate matrices have a special place among porous structures [1]. At present time, application of nanoporous silica matrices mainly related to the transparency of these glasses in the visible spectral range and to the possibility of obtaining samples of optical quality [2].
The research of nanoporous matrices occupies a certain place in the life of science community. To obtain a material which will possess the specified properties it is important to develop technology that will include comprehensive researches for estimation of quality of the product.
The aim of this work was to research the influence of each stage of chemical processing on the final optical heterogeneity of the sample.

2. Materials and method
In the experiment we used nanoporous silicate matrices that were made of sodiumborosilicate two-phase glass formed by two interpenetrating phases: chemically unstable borate and chemically stable silica. We used matrices in the form of polished disks with a diameter of 15 mm and with a thickness of 1 mm and in the form of plane-parallel plates, which were made using proven technology from two-phase glass DV-1 after stage of heat processing.
The main characteristics of the samples during their development are the average pore diameter and the free pore volume, characterizing the volume of the sample that isn’t occupied by silica frame. The average pore diameter of the samples is 17 nm. The free pore volume of such samples is in the range of 48-58% and depends on the time of the procedure of alkaline etching. During developing nanoporous silica matrices technological regulation was observed and it gave an ability to reproduce the specified characteristics of NPM from batch to batch.
Control of phase homogeneity of the samples was carried out at each stage of processing by carrying out researches of samples on the stand of DHI – scheme of the stand (figure 1) - in the initial state,
after acid etching and after alkaline etching. Digital interferograms of the samples were obtained and then they were analyzed.

![Figure 1. Experimental stand for the research of transparent objects by method of digital holographic interferometry: 1 - the probe laser; 2a, 2b - beamsplitter cubes; 3 - collimator; 4 - object of research; 5 - rotary mirror system; 6 - lens 1; 7 - aperture diaphragm; 8 - lens 2; 9 - CMOS-matrix; 10 - DPSS laser (532 nm); 11 - device OPHIR.](image)

An additional problem of the research was to determine the influence of gravity on the result of the procedure of chemical processing. During setting to a chemical processing the samples were oriented so that the action of gravity relative to the sample was always pointing in the same direction. In order to determine the influence of gravity on the result of the etching before alkaline etching sample 1 was rotated on 180° relative to the horizontal axis and sample 2 was left in the same position.

As the main parameter for estimation of optical heterogeneity was used the effective refractive index $n_{\text{eff}}$ and its changes throughout the volume of the sample.

The effective refractive index is determined as following:

$$n_{\text{eff}} = V_1 n_1 + V_2 n_2,$$

where $V_1$ – the relative free pore volume; $n_1$ – the refractive index of the immersion of free pore volume (air immersion – $n_1=1$, water immersion – $n_1=1.33$); $V_2$ – the relative volume of sample that is occupied by the frame SiO$_2$; $n_2$ – the refractive index of the sample frame ($n_2=1.45$).

Calculation of the free pore volume was carried out by the weight method which was proposed in the following work [3].

The effective refractive index of the sample calculated by the formula 1 represents by itself a refractive index averaged throughout the volume of the sample.

In table 1 the parameters of the obtained matrices during filling of pores with air and water after each stage of chemical etching are shown.

| Sample | Stage 1 | Stage 2 |
|--------|---------|---------|
|        | $V_1$,% | $n_{\text{eff}}(n_1 = 1)$ | $n_{\text{eff}}(n_1 = 1.33)$ | $V_1$,% | $n_{\text{eff}}(n_1 = 1)$ | $n_{\text{eff}}(n_1 = 1.33)$ |
| 1      | 22.56   | 1.35    | 1.42   | 54.31 | 1.20   | 1.38   |
| 2      | 22.64   | 1.34    | 1.42   | 53.88 | 1.20   | 1.38   |

Table 1. Parameters of the obtained matrices during filling of pores with air and water after acid (stage 1) and after alkaline (stage 2) etching.
3. Results and discussion

Interferograms characterizing the phase structure of the initial samples were obtained. The samples were set in a cuvette which was included in the stand of DHI.

Table 2. Phase structure of billets for disks samples which was measured in the air (left) and in the water (right).

| Sample | In the air | In the water |
|--------|-----------|-------------|
| 1      | ![Interferogram](image1.png) | ![Interferogram](image2.png) |
| 2      | ![Interferogram](image3.png) | ![Interferogram](image4.png) |

Optical heterogeneity of the samples after chemical processing due to the uneven distribution of the free pore volume throughout the volume of the sample. Meanwhile the thickness of the sample 1 doesn’t change. Estimation of uneven of the initial billets of samples 1 and 2 (column 3 of table 2) and samples 1 and 2 after all stages of chemical etching (column 6 of table 3) in water immersion ($n_f=1.33$).

Interferograms characterizing the phase portrait of the sample are shown in table 2 for the initial state of researched disks sample before chemical etching. In this case, the observed interference fringes with the same period $d$, indicate about insignificant wedging of the samples (dotted line on figure 2).

Interferograms of samples 1 and 2 after each stage of etching are shown in table 3 and they show optical heterogeneity – the distance $d$ between two adjacent fringes is changed in the vertical direction (section A-A coinciding with the direction of gravity), this suggests that these changes are due to the influence of gravity on diffusion chemical processes.

The distance between two interference fringes corresponds to a phase difference of $2\pi$. Thus, in the centre of the sample changes of phase of $2\pi$ happens on the section $\Delta z = d = 5$ mm, and at the top of the sample on the section $d = 0.2$ mm, where $d$ is the distance between two interference fringes. It is the value $\Delta n/d$, which characterizes the optical heterogeneity of the sample, the effective refractive index which, as a rule, is averaged throughout the volume.
Table 3. Phase structure of samples after two stages of technological processing.

| Sample | After stage 1 in the air | After stage 1 in the water | g (z) | After stage 1 in the air | After stage 1 in the water | Δn/d, mm⁻¹ |
|--------|--------------------------|---------------------------|-------|--------------------------|---------------------------|-------------|
| 1      | Top                      | Top                       |       | Bottom                   | Bottom                   | 8x10⁻⁵      |
|        | Bottom                   | Bottom                   |       | Top                      | Top                      | 18x10⁻⁴     |
| 2      | Top                      | Top                       |       | Bottom                   | Bottom                   |             |
|        | Bottom                   | Bottom                   |       | Top                      | Top                      |             |

Figure 2. The change of the value Δn/d, in the section of samples 1 and 2 along the line A-A (table 2 and 3), dotted line – billets in water, solid lines - the samples after all stages of chemical etching in water.

4. Conclusion

Optical heterogeneity of the samples due to the influence of chemical etching is associated with the removal of the soluble phase that is enriched with the oxides of boron and sodium during acid etching and with the removal of “secondary” silica from the area of destruction of borate phase during alkaline etching.

The change of the optical heterogeneity is associated with the orientation of the samples in the gravity field and its value is 8x10⁻⁵ in the center and 18x10⁻⁴ on the edge of the sample 1. During turning of the sample before alkaline etching there is a shift to the center, while in the sample that wasn’t turned over there is only a gain of heterogeneity obtained during acid etching.
References

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