# Characterisation of the inner structure and surface of nanoporous sodium-borate-silicate glasses

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Results of investigations are reported which have been carried out with use of some physical and chemical techniques on the nanoporous sodium-borate-silicate glasses with pore sizes within 5–100 nm. Porous structure is formed due to the leaching-out of initial glass Na 7/23 with phase separation. Some important parameters of the vitreous framework have been determined: percentage distribution of pores sizes, fractal dimensionality of porous glass, crystallinity grade within vitreous bulk, phase composition of crystalline areas within silica framework. The survey of the measured spectral characteristics (mainly in the infrared wave range) of the porous glass surface and its interpretation are presented. Spectral behaviour of some species immobilised on the surface of nanopores is discussed. Interaction of the silica surface, adsorbates and ambient gas medium is interpreted on the basis of the Pearson–Lewis conception about hard and soft acids and bases.

Keywords: nanoporous glass, X-ray phase analysis of microcrystals, gas adsorption, surface adsorption sites, characteristic IR spectra of the glass surface.

## 1. Introduction

Nanoporous sodium-borate-silicate glasses are known to serve as an optimum substrate for various molecular species demonstrating some specific features in the adsorption state [1, 2]. Such materials open a broad practical application areas in catalytic processes [3, 4], in fluorescent and colourimetric gas indication [5, 6], *etc*. So, further investigations are needed of the structure and contents of both the porous matrix and the particles embedded therein.

In addition to the known routine methods of porous structure characterisation, an X-ray diffractometry is most useful here. Some X-ray researches on nanoporous materials have been carried out [7, 8] but they are rather few, so that each kind of porous material is to be investigated anew in order to determine the parameters of porous structure, crystallinity grade within vitreous framework, phase content of crystallites, spectral characteristics, *etc*.

Of special interest is an identification of the adsorption sites on the highly developed and irregular inner pore surface. In this connection, the simple gas molecules may serve as molecular probes, the gas molecules being electrophilic or nucleophilic in their nature. Interaction of the probe molecules with specific adsorption sites may be revealed with use of molecular infrared spectroscopy. The first steps have only been undertaken in this direction [6, 9, 10], so further investigations are needed and the relevant conceptions are to be offered.

## 2. Experimental section

### 2.1. Sample preparation

The sample sizes were usually of $8\times8\times1$ mm. The composition of the matrix glass before its chemical treatment was (mass%): $Na_2O$ – 7, $B_2O_3$ – 23, $SiO_2$ – 70. Electron probe microanalysis of the original non-porous glass had shown the $Na_2O$ content being approximately of 6.5%. After the glass leaching-out (in the 3 M HCl), the $Na_2O$ content decreased down to 0.2%, the $SiO_2$ content was 87.5%. So, the calculated $B_2O_3$ content remained at the level of about 13%, probably because of lower solubility of sodium borates.

Finally, the structure was stabilized by the sample annealing in air at +500°C during 1 hour.

When required, the samples were prepared by impregnating the original mesoporous matrix in liquid solutions of specific substances and then applying the drying procedure in order to remove the solvent, so that dissolved molecules remained physically adsorbed on the matrix pore surface.

### 2.2. X-ray measurements

For X-ray analysis a diffractometer D/MAX-RB with accessories was used (Rigaku Corp., Japan, [11]). The X-ray source was a 12 kW rotating (6000 rpm) anode (Cu) generator. The diffractometer comprises a convex diffracting crystal monochromator in combination with the wide-angle goniometer and scintillation counter. The measurements and data analysis proceeded with use of specialised purpose-aimed PC. The instrument provided measurements in both small-angle (0.05–0.40°) and wide-angle ($2\theta$-angle from –3° till 145°) ranges.

After smoothing, elimination of background and $K\alpha_2$ stripping, the software made routines for peak finding and for phase identification by a search match procedure using database of the Joint Committee on Powder Diffraction Standards (JCPDS) [12].

The results were presented as a list of possible compounds accompanied by a number of corresponding JCPDS cards. The possible phases were arranged with respect to a calculated value of the reliability factor (RF) which indicated the matching accuracy of the experimental patterns with the standard ones from the database. The matching proceeded with taking into consideration both position $d$ and intensity $I$ of the peaks compared [11].

## 2.3. Spectral measurements

Spectral measurements in the infrared wave range were made with the use of advanced IR Fourier-transform spectrometer 5DXB (Nicolet, USA) [13] which was most suitable for spectra of samples having optical density up to 4 and higher.

Visible absorption spectra of the samples and of the impregnating solutions were measured by the spectrophotometer СФ-26 (LOMO Corp., Russia) within the wave range of 300–800 nm. In order to compensate for the light scattering caused by the porous matrix, a "clean" porous sample was measured as a reference sample.

In the course of experiments the samples were fixed in a holder placed within a pumpable cell being transparent to light. A gas mixture of desired content might be admitted into cell and the spectral transmittance might be measured.

Before being characterized, the samples were kept in a selected gas mixture for a sufficiently long time (30 min or longer). The reference spectral characteristics relate to samples having been kept in normal laboratory atmosphere with relative humidity of 50% at 20°C.

## 3. Results and discussion

An appropriate processing of the adsorption isotherms in the area of capillary condensation has revealed the pore size distribution in vicinity of 8 nm (mesoporous glass) and 80 nm (microporous glass); the porosity grade to respectively 28% and 45% of the total sample volume. The specific area was calculated at a specific point $B$ of the isotherm curve knee. The values obtained were about 100 $m^2/cm^3$ for the mesoporous glass and 8.5 $m^2/cm^3$ for the microporous glass.

Mesoporous glass (8 nm) showed a clear isotherm of type IV (an $A$-subtype), according to Gregg's classification [14]. This reveals the long-capillary shape of pores with open ends. The scanning electron microscopic photographs with magnification scale up to ×60 000 apparently demonstrate the channel-shaped pore structure.

The more detailed data were obtained with the use of techniques and facilities of small-angle X-ray scattering. This allowed measurement of the pore size distribution just in the range of 1–1000 nm. The method was based on the processing of scattering function $I_s$ upon a gyration radius $R_0$ [11]. According to Guinier's theory, the signal intensity $I_s$ is proportional to the scattering vector $S^2$. So, the radius of the sphere attributed to the element structure may be calculated as $R = 1.29 R_0$.

The results obtained are given in Fig. 1. One can see that characteristic radius $R$ of the structure elements within small-porous glass is of 93.88 nm as practically mono-dispersion size distribution (Fig. 1**a**). In contrast to that, three characteristic size values have been found for the large porous glass: 209.45 Å (35.8%), 488.60 Å (25.2%) and 858.27 Å (39.1%), see Fig. 1**b**.

Small-angle X-ray techniques and facilities may also provide information about fractal dimensionality $D$ of porous structure derived from the function $I_s = k S^D$. The fractal dimensionality $D$ values were found to be 1.8 for microporous glass and
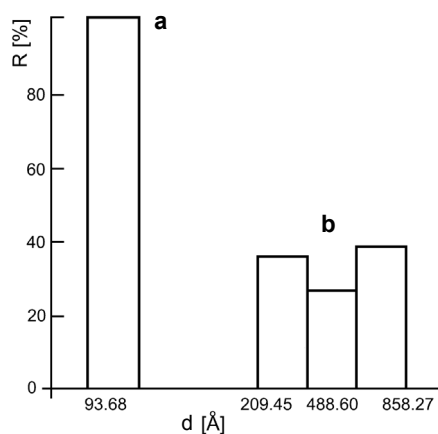
Fig. 1. Pores size distribution within small (**a**) and large (**b**) porous samples.

2.0 for mesoporous glass, the latter value testifies to the inner surface of the sample being essentially plane, *i.e.*, two-dimensional.

Phase content was determined with the use of wide-angle X-ray techniques. The silica matrix is known to be predominantly amorphous, the X-ray spectra of samples show a broad maximum corresponding to the vitreous state of matter. Some additional information was obtained using computer processing of the patterns. The crystallinity grade in accordance with Ruland's method [15] was found to be about 7% for the mesoporous glass and 9% for microporous glass. That is why the RF values for the porous samples were in some cases rather low. Nevertheless the obtained data as a whole seem to be reliable enough.

The prevailing silica phase being in the microporous glass was Tridimite (JCPDS card No. 270605), RF = 461.

The prevailing crystal phases of silica in mesoporous glass were SilicaX (No. 120708) with RF = 49 and Low Syngony phase (No. 160380), RF = 47. The sodium borates and silicates were present, too.

A course visible adsorption spectrum of original mesoporous samples in normal atmosphere demonstrated usual continuous drop in accordance with Rayleigh's law. Much more informative, however, are the infrared spectra.

Porous glasses have been spectrally investigated in the infrared wave range by many researchers all over the world for the last several decades. Noteworthy is that those have dealt with thoroughly dried and evacuated samples, usually at elevated temperature, the samples under such conditions being sufficiently transparent in this wave range. In contrast to that, our investigations have been aimed at the spectral behaviour of porous samples in actual humid atmosphere, so that the sample surface was significantly hydrated. Formerly, the infrared range was not accessible for measurements because the adsorbed water molecules caused a strong absorption. We have solved this problem with use of the up-to-date Fourier-transform spectrometer.
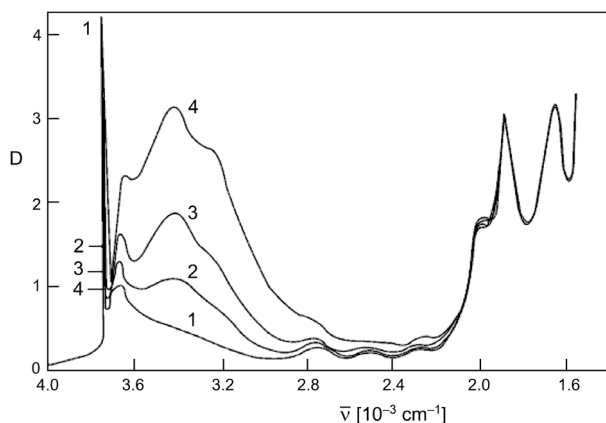
Fig. 2. Absorption spectra of mesoporous glass during its rehydratation after thermal treatment at 500°C (1 hour): 1 – after 10 s, 2 – after 5 min, 3 – after 15 min, 4 – after 60 min.

The infrared spectra of the mesoporous samples at different temperatures are given in Fig. 2.

A prominent line at 3750 cm$^{-1}$ for the dried samples is certainly attributed to the vibrations of isolated OH-groups being linked to the surface [9]. Their revelation in spectra of hydrated samples testifies to the presence of comparatively small pores with sizes of less than 8 nm, where the free vibrations of single OH-groups may occur. A faint band around 3655 cm$^{-1}$ may be attributed to the stretching vibrations of shared pairs of OH-groups in adjacent positions within water molecules Si–O–[H---O–H], being directly bound to the pore surface (through its O–Si–O–Si–O framework). That kind of water may be removed only by heating the sample above 700°C. This process is irreversible by nature. When annealing the samples up to 500°C, this band remained in spectrum, however, significantly weakened. In the course of free cooling of the sample in ambient atmosphere, this band is slowly restored but the growing absorption band assigned to the physically adsorbed water soon overtakes it.

Molecules of water layer covering the surface over the hydroxyl groups cause a broad band with maximum at 3430 cm$^{-1}$. Several bands at frequencies below 2000 cm$^{-1}$ are due to vibrations of the Si–O structural groups of silica network and to the bending vibrations in the molecules of water layer.

Due to highly developed surface of samples its spectra are effectively influenced by the components of ambient atmosphere, as is shown in Fig. 3. Of special importance and interest is the fact that different gas molecules exert influence on the spectra in different ways [10]. Ammonia vapours act as smoothing agent (see spectrum 5) due to formation of hydrogen bound all over the sample surface with participation of ammonium ions ($NH_4^+$) adsorbed on the Si–OH groups. These are Brønsted's sites. At the same time there is a strong band in the spectrum (with maximum at 3000 cm$^{-1}$)
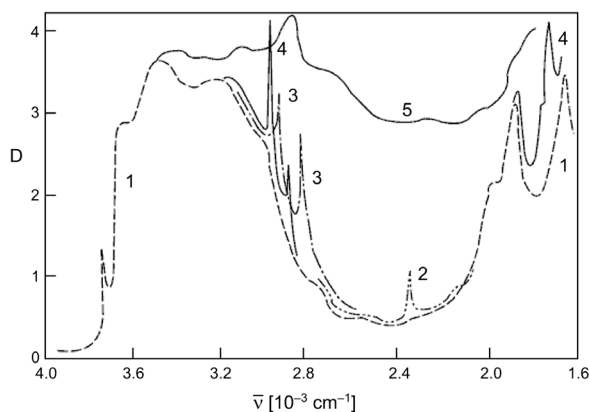
Fig. 3. Absorption spectra of mesoporous glass under different atmospheric conditions: 1 – air with relative humidity of 50% at 20°C, 2 – air and carbon dioxide (10% vol.), 3 – air and methanol vapours (10% vol.), 4 – air and acetone vapours (10% vol.), 5 – air and ammonia vapours (10% vol.).

assigned to the vibrations of adsorbed molecular ammonia ($NH_3$) which demonstrates the presence of the surface sites of Lewis' type. On the other hand, the carbon dioxide, methanol and acetone vapours also produce the clearly distinct peaks (spectra 2–4) being attributed to the valence and bending vibrations within immobilised molecules. These peaks are slightly shifted with regard to the spectra of isolated molecules. The above mentioned spectral changes were found to be more or less spontaneously reversible. Hence, an interaction between molecules immobilised on the surface and molecules of gas may be characterised as a physical adsorption.

So, the infrared spectral data confirm a conception about two surface adsorption sites being referred to as Brønsted's and Lewis' sites, respectively. Noteworthy is the fact that the spectra have been measured on the samples being in the normal humid atmosphere, at the sample surface being substantially hydrated.

The immobilised molecules turned out to be sensitive to the underlying surface state and mostly interactive to the gas molecules from ambient medium (see [6]). So, the immobilised indicator molecule and adsorbed gas molecule form more or less stable complex on the pore surface.

It has been found that not only the organic colour acid-based indicators but also some transition metal ions ($Co^{2+}$, $Cu^{2+}$, $Pd^{2+}$), being immobilised on the pore surface, may form the complexes with certain gas molecules accompanied by the specific colour changes.

For systematisation and interpretation of these phenomena a Lewis' and Pearson's conception about hard and soft acids and bases (HSAB) has been invoked [16, 17]. According to the HSAB conception, all the Lewis' acids and bases (electrophilic and nucleophilic agents, respectively) may be characterised upon its ability to form the stable acid – basic complexes in the course of the electrophilic (nucleophilic)

T a b l e. Characteristics of the component hardness/softness and stability of the surface complexes. Time constants (min) of the complex formation/destruction are given in parentheses; HB – hard base; SB – soft base; HA – hard acid; SA – soft acid; HSA – intermediate acid; Ind – anionic colour indicator; Phpht – phenolphtalein; Brmcrs – bromocresol purple.

| Adsorbent \ Adsorbate | $H_2O$ HB | $CH_3OH$ HB | $NH_3$ HB | CO SB | $CO_2$ HA |
|---|---|---|---|---|---|
| Dehydrated surface of mesoporous glass ($SiO_2$)–HA | Stable (> 300) | Stable (> 300) | Stable (> 300) | Unstable (15) | Unstable (5) |
| Hydrated surface of mesoporous glass (Si–OH + $H_2O$)–HB | Unstable (10) | Unstable (10) | Unstable (10) | — | Unstable (10) |
| Hydrated surface of mesoporous glass + Ind⁻(Phpht)–SB | — | — | Unstable (3) | — | Unstable (10) |
| Hydrated surface of mesoporous glass + Ind⁻(Brmcrs)–SB | — | — | Unstable (3) | — | Unstable (3) |
| Hydrated surface of mesoporous glass + $Co^{2+}$–HSA | Stable (20) | Stable (20) | Stable (30) | — | — |
| Hydrated surface of mesoporous glass + $Cu^{2+}$–HSA | Stable (300) | Unstable (10) | Stable (300) | — | — |
| Hydrated surface of mesoporous glass + $Pd^{2+}$–SA | — | — | — | Stable (30) | — |

substitution reactions. A characteristic parameter here is the rate of the complex formation.

Due to the numerous studies it has been found that the ions such as $H^+$, $Na^+$, $Ca^{2+}$, $Si^{4+}$, *etc.*, and some oxides including $CO_2$ and $SiO_2$ play a role of the hard acids. The $Pd^{2+}$, $Ag^+$ ions as well as neutral metal atoms may be assigned to the soft acids. Such ions as $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$ and others take an intermediate position.

On the other hand, the hard Lewis' bases are the $OH^-$, $CO_3^{2-}$, $SO_4^{2-}$ ions and the $H_2O$, $NH_3$, $N_2H_4$ molecules. The soft bases are the molecules CO, $(CH_3)_2SO$, the $I^-$ ion and others, in the intermediate group fall, for example, the $Br^-$, $SO_3^{2-}$ and $NO_2^-$ ions.

Pearson formulated and substantiated the following laconic principle: *Hard acids preferably do compounds with hard bases and soft acids with soft bases, otherwise the stable compounds and strong bonding do not formed* [16].

The Lewis–Pearson's conception is very useful and productive in many cases, however, it has till now a rather qualitative character and needs further proves. Our experimental results most likely present one of such proves. Indeed, in the Table the chemical systems investigated are arranged according to hardness and softness of its components and stability of the formed complexes, the complex stability being associated with a time constant of the sample colour change after gas component appearance/disappearance in the ambient atmosphere. As one can see, in most cases of interactions the above mentioned principle of Pearson is obeyed and substances

being opposite in their nature form more stable complexes and *vice versa*. This phenomenon may be particularly used for the development of colourimetric gas sensors [6].

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