

# Studies on the inner structure of porous sodium-borate-silicate glass and some clusters formed therein

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The nanoporous sodium-borate-silicate glasses Na 7/23 (standard symbol) with pore sizes within 5–100 nm have been investigated. The X-ray investigations in wide and small angles allowed us to determine some important parameters of glassy framework: percentage distribution of pore sizes being in the vicinity of 8 nm and 80 nm; fractal dimensionality of porous glass being of 2.0 (8 nm pores) and 1.81 (80 nm); crystallinity grade within vitreous bulk being of 7% (8 nm) and 9% (80 nm); phase composition of crystalline areas within silica framework. The nanoclusters of crystallohydrates on the basis of cobalt(II) chloride supported on the inner surface of nanopores have been characterised, too.

## 1. Introduction

The nanoporous sodium-borate-silicate glasses are known to serve as a substrate for various molecular species showing some specific features in adsorption state. Such materials open up a broad practical application area in catalysis processes [1]–[3], in fluorescent and colorimetric gas indication [4], [5], *etc.* So, further investigations are needed on the structure and contents both of the porous matrix and the particles imbedded therein.

Some X-ray researches on nanoporous materials have been carried out [3], [4], [6], [7] 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.

On the other hand, there is a steadily growing interest in materials being manufactured as powders or separate particles of high dispersion grade [8]–[10]. There are many problems relating to the properties and behaviour of metal complexes being in highly dispersed state [1], [2], [11]. For the present investigation the cobalt(II) chloride crystallohydrates as an ultradisperse phase were chosen, because they have wide application as colour indicators of temperature and humidity. In addition, the cobalt(II) chloride is a convenient reference compound, inasmuch as its properties and structure have been thoroughly studied [12].

## 2. Experimental

### 2.1. Sample preparation

The matrices were made of porous silica glass prepared by means of the well-known thermal and leaching-out procedures on the phase-separated silica glass [13], [14], [15]. The sample sizes were usually  $8 \times 8 \times 1$  mm. According to Russian standard, the glass composition before its chemical treatment was:  $\text{Na}_2\text{O}$  — 7 mass %;  $\text{B}_2\text{O}_3$  — 23%,  $\text{SiO}_2$  — 70%. The electron probe microanalysis of initial non-porous glass showed the  $\text{Na}_2\text{O}$  content to be approximately 6.5%. After leaching-out the alkaline phase of the initial glass the  $\text{Na}_2\text{O}$  contents decreased to 0.2%.

The procedure for impregnation of the porous matrix with cobalt chloride was as follows. The porous samples were put into saturated aqueous solution of  $\text{CoCl}_2$  for 12 hours at  $+85^\circ\text{C}$ , the solution being in the labile region of the solubility curve. After this procedure, the samples were taken out of the solution and dried in air at  $+90^\circ\text{C}$  for 1 hour, then left open in laboratory for one day, the relative air humidity being about 50% ( $+20^\circ\text{C}$ ). Then the sample surface was carefully cleaned for removal of surface layers. The first series of measurements was carried out without any additional thermal treatment, the second one — after annealing at  $+250^\circ\text{C}$  for 1 hour. For the reference measurements the initial powder reagent  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  was ground and sieved to 270 mesh.

### 2.2. X-ray measurements

For X-ray analysis a diffractometer D/MAX-RB with accessories was used (Rigaku Corp., Japan, [16]). The measurements and data analysis were made using specialised PC. The instrument provides measurements both in small-angle ( $0.05$ – $0.40^\circ$ ) and in wide-angle ( $2\theta$ -angle from  $-3^\circ$  to  $145^\circ$ ) ranges. In the small-angle mode the scanning proceeds with a speed of  $0.01^\circ/\text{min}$ , a scanning step being of  $0.001^\circ$ . In the wide-angle mode the patterns are recorded during continuous scanning with a speed of  $10^\circ/\text{min}$ , the step of scanning being of  $0.02^\circ$ . The software makes routines for peak finding and for phase identification by search match procedure using database of Joint Committee on Powder Diffraction Standards (JCPDS) [17]. The results are presented as a list of possible compounds accompanied with numbers of the corresponding JCPDS cards. The possible phases are arranged in respect of a calculated reliability factor (RF), which indicates the matching accuracy of the experimental patterns to the standard ones from the database. The matching proceeds taking into consideration both position  $d$  and intensity  $I$  of compared peaks [16]. The maximum possible value of RF is 1000.

## 3. Results and discussion

### 3.1. Porous matrices

An appropriate processing of adsorption isotherms taken in the area of capillary condensation has revealed the pore size distribution in the vicinity of 8 nm and

80 nm, the volume porosity being of 28% and 45%, respectively. The corresponding radii determined by means of mercury porometry are about 8 nm and 100 nm. Specific area was calculated upon a specific bending point in the isotherm curve. The values found were  $100.6 \text{ m}^2/\text{cm}^3$  (8 nm) and  $8.6 \text{ m}^2/\text{cm}^3$  (80 nm). The small-porous glass shows the isotherm of IV type (A-subtype) according to a Gregg's classification [18]. That corresponds to the long-capillary shape of pores with open ends. The scanning electron microscopic pictures taken with magnification scale up to  $\times 60\,000$  really demonstrate the channel-shaped pore structure with approximately the same pore sizes.

The more detailed data have been obtained with the use of techniques and facilities of small-angle X-ray scattering. It allows the pore size distribution to be measured just in the range of 1 – 1000 nm. The method is based on the processing of scattering function  $I_s$  upon a giration radius  $R_0$  according to the Guinier's theory [16]. A characteristic radius of the structure elements within small-porous glass is of 93.88 nm as practically monodisperse size distribution. For the large porous glass three characteristic size values have been found: 209.45 Å (35.8%), 488.60 Å (25.2%) and 858.27 Å (39.1%).

Small-angle X-ray techniques and facilities may also provide information of the fractal dimensionality  $D$  for the porous structure derived from the plot of function  $I_s = k \cdot S^D$ . The fractal dimensionality values found were 1.81 for microporous glass and 2.0 for mesoporous glass, the latter value giving evidence of the inner surface of the small-porous sample being essentially plane.

Phase content was determined with the use of wide-angle X-ray techniques. The silica matrix is known to be mainly amorphous, the X-ray spectra of samples show the broad maximum corresponding to the vitreous state of matter (see Fig. 1d). Some additional information was obtained from the computer processing of patterns. The crystallinity grade in accordance with Ruland's method [19] 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 rather low. Nevertheless, the obtained data seem to be reliable enough. The prevailing crystal phases of silica in mesoporous glass were SilicaX (JCPDS card No. 120708) with RF = 210 and Low Syngony phase (No. 160380), RF = 150. The sodium borates and silicates were present, too. The prevailing silica phase found in microporous glass was Tridimite (No. 270605), RF = 280.

### 3.2. Immobilised clusters

Experimental X-ray patterns for the samples under study are displayed in Fig. 1. Computer data processing allowed us to distinguish series of the peaks which relate to the crystallohydrates grown up in the pores.

Assignment and interpretation of experimental patterns for the powdered reagent  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (Fig. 1a) presents no difficulties. After thermal treatment the crystallohydrates loose the water and transform into dihydrates and waterless  $\text{CoCl}_2$  (Table).

The patterns for the ultradispersed crystallohydrates within porous matrix are much more complicated (Fig. 1b,c). An example of experimental and standard

**Table.** Identified compositions and phases found in the dispersed crystallohydrates ranged over the RF (in parentheses are the card numbers of the JPCDS standard samples).

In powder (particle sizes of 5 $\mu\text{m}$ )		Within porous matrix (pore sizes of 80 nm)		Within porous matrix (pore sizes of 8 nm)	
Chemical formula	RF	Chemical formula	RF	Chemical formula	RF
Before thermal treatment					
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (290466)	659	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (30786)	317	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (30786)	369
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (130339)	398	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (250242)	231	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (290466)	136
$\text{CoCl}_2 \cdot \text{H}_2\text{O}$ (230933)	62	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (230933)	227		
$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (30786)	61	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (251039)	181		
After thermal treatment at +250 °C					
$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (250242)	444	$\text{CoCl}_2$ (220590)	477	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (250242)	286
$\text{CoCl}_2$ (220590)	372	$\text{CoCl}_2$ (150381)	453	$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (290466)	247
$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (30786)	307	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (30786)	422	$\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ (30786)	160
$\text{CoCl}_2 \cdot \text{H}_2\text{O}$ (150381)	228	$\text{CoCl}_2 \cdot \text{H}_2\text{O}$ (250242)	292		
$\text{CoCl}_2 \cdot \text{H}_2\text{O}$ (230933)	110				

JCPDS patterns is given in Fig. 2. The computing search match procedure results in printing a list of phases ranging over RF value. Results of the data processing are listed in the Table.

For the initial reagent, two phases of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  were found, the predominating one (card No. 290466) being monoclinic  $I2/m$ . The probability of crystallohydrates occurring with lower water contents was insignificant. Heating of the initial powder up to +250 °C causes total decomposition of hexahydrates with formation of dihydrates and waterless compositions. The predominating phase here is mono-

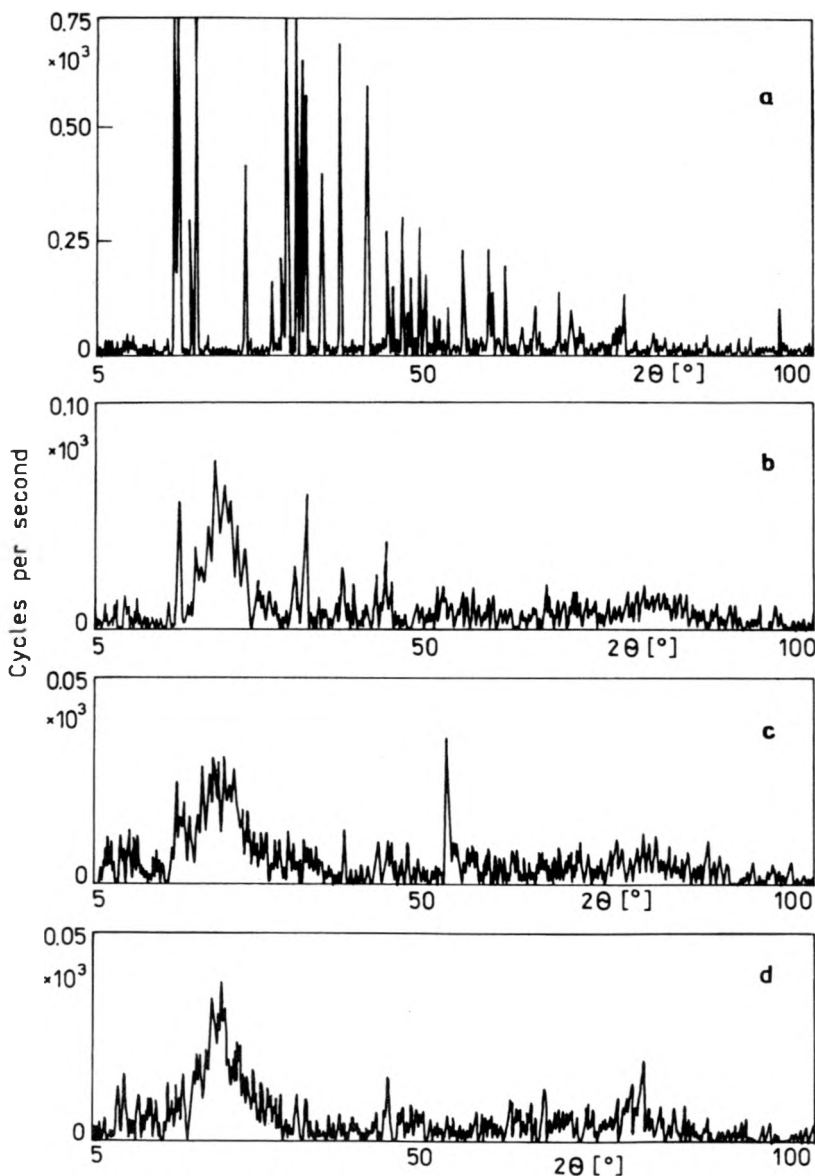


Fig. 1. Experimental X-ray patterns (after the previous computer processing): **a** – powder of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ , **b** – crystallohydrates in matrix with pore sizes of 80 nm, **c** – crystallohydrates in matrix with pore sizes of 8 nm, **d** – “empty” matrix with pore sizes of 8 nm.

clenic dihydrate (250242),  $C2/m$ , with angle  $\beta = 97.55^\circ$ . The data obtained with the use of the initial reagent as a reference sample confirm that, in spite of the probabilistic nature of the phase identification process, the computer search match results presented in the Table are reliable enough (the maximum value of RF value is 1000).

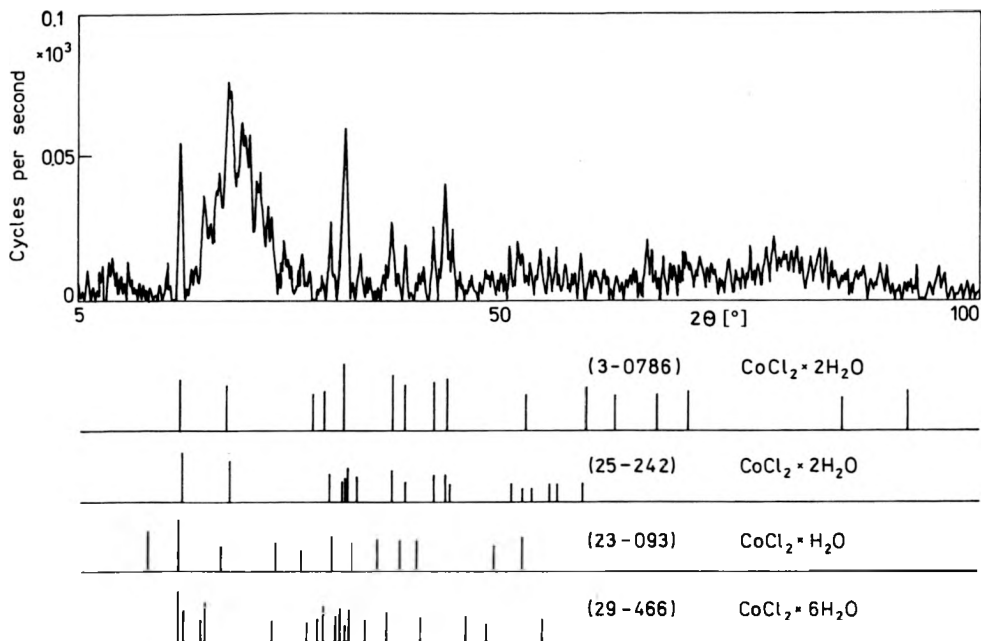


Fig. 2. Experimental pattern according to Fig. 1 b, and standard JCPDS patterns for the phases found in porous sample with pore sizes of 80 nm.

Some important results have been obtained for cobalt chloride crystallohydrates grown in the pores. The data shown in the Table indicate with sufficient reliability (RF = 136–477) the presence of crystalline particles within the pores not only of 80 nm but also of 8 nm. Taking into account the fact that the porous samples remain permeable after impregnation, the crystallite sizes are apparently much less than 8 nm. It is noteworthy that the hexahydrate does not disappear after technological treatment of samples at +85 °C.

Heating of porous (80 nm) samples up to +250 °C leads to dehydration of cobalt chloride, meanwhile the dihydrates partly remain in the pores of glass.

Some peculiar features are found in the small-porous samples. At first there is relatively high content of crystalline dihydrate in the pores. Secondly, it is mostly surprising that the hexahydrate phase (290466) was conserved after thermal treatment at +250 °C, the amount of hexahydrate being of the same order of magnitude as the dihydrate.

It is noteworthy that, despite the tiny sizes of crystalline particles and destructive influence of the powerful surface fields, the results obtained indicate the presence of undistorted crystallohydrates, since the search match procedure proceeds in relation to the regular bulk crystals.

The results obtained in the present paper could be applied to developments in technology of the humidity and temperature sensors.

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