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Connectivity of glass structure. Oxygen number

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Abstract. With reference to mathematics, crystal chemistry and chemical technology of synthesis of glass structures in the solution (sol-gel technology), the paper is devoted to the study of the degree of connectivity of a silicon-oxygen backbone (f_{Si}) and the oxygen number (**R**) [1]. It reveals logical contradictions and uncertainty of mathematical expressions of parameters, since f_{Si} is not similar to the oxygen number. The connectivity of any structure is a result of various types of bonds: ion-covalent, donor-acceptor, hydrogen bonds, etc. Besides, alongside with SiO_2 , many glass compositions contain other glass-forming elements due to tetrahedral sites thus formed. The connectivity function of a glassy network with any set of glass-forming elements is roughly ensured by connectivity factor Y [2], which has monovalent elements loosening a glassy network. The paper considers the existence of various structural motives in hydrogen-impermeable glasses containing B_2O_3 , Al_2O_3 , PbO , Na_2O , K_2O and rare-earth elements. Hence, it also describes gradual nucleation, change of crystal forms, and structure consolidation in the process of substance intake from a matrix solution according to sol-gel technology. The crystal form varied from two-dimensional plates to three-dimensional and dendritical ones [3]. Alternative parameters, such as the oxygen number (**O**) and the structure connectivity factor (**Y**), were suggested. Functional dependence of $Y=f(O)$ to forecast the generated structures was obtained for two- and multicomponent glass compositions.

1. Introduction

Any law, hypothesis, or formula are merely the model with some degree of objective reality. In a real world, things are much more complex and diverse. In the process of new knowledge accumulation, any doctrine is a direct way to stagnation and regress. The revealed contradictions in subjects of the research shall be considered not only as denial of previous ideas but, first of all, as internal sources of steady development. This is a natural dialectic of knowledge [1, 4].

This work presents the critical analysis of such known parameters as the degree of connectivity of a silicon-oxygen backbone (f_{Si}) and the oxygen number (**R**) being essential for the glass science [5].

2. Materials and methods

Work [5], the classical status of which is not disputable, renders the following: “... SiO_2 exists in glass in the form of tetrahedrons [SiO_4] of different types. Such tetrahedrons shall have different properties, first of all, depending on the quantity of Me_2O and MeO components in glass, since bridge (“doubly-connected”) oxygen differs in properties from non-bridge (“singly-connected”) oxygen. In other



words, properties $[\text{SiO}_4]$ of tetrahedrons shall primarily depend on the degree of connectivity of a silicon-oxygen backbone. The measure of the degree of connectivity is a f_{Si} coefficient equal to the relation of the number of silicon atoms to the number of oxygen atoms Si/O, or a reciprocal value, i.e. the oxygen number $\mathbf{R} = \frac{\text{O}}{\text{Si}}$. The f_{Si} coefficient is calculated according to the following formula:

$$f_{\text{Si}} = \frac{\gamma_{\text{SiO}_2}}{\gamma_{\text{Me}_2\text{O}} + \gamma_{\text{MeO}} + 3\gamma_{\text{Me}_2\text{O}_3} + 2\gamma_{\text{MeO}_2} + 5\gamma_{\text{Me}_2\text{O}_5} + 3\gamma_{\text{MeO}_3}}, \quad (1)$$

where γ [gamma] – mol fraction of the corresponding oxide specified in the suffix.

In expression (1), SiO_2 oxide is opposed to other oxides, potential glass components. Obviously, it deals with compositions where SiO_2 oxide is the main glass-forming element. Such glass-forming elements as B_2O_3 , GeO_2 , P_2O_5 , Al_2O_3 , BeO , etc. are presented in denomination as oxygen donors for the formation of a siliceous structure. How can this be justified?

Expressions for parameters \mathbf{R} and f_{Si} are illogical. By their definition, \mathbf{R} and f_{Si} represent the relation of “the number of silicon atoms to the number of oxygen atoms”. It is claimed without evidence that \mathbf{R} and f_{Si} are inversely related to each other. The f_{Si} parameter is the relation of oxide concentration (1), i.e. it is not the relation of the number of silicon and oxygen atoms. Connectivity is a result of various types of bonds: ion-covalent, donor-acceptor, hydrogen bonds, etc.; number \mathbf{R} is a quantitative characteristic of oxygen content in a system [5]. Thus, connectivity is not identical to the oxygen number.

Since the study deals with the number of atoms, it may be assumed that all components specified in expression (1) contain one mol – $\gamma=1$. Taking into account the percentage of elements (Si, Me) and oxygen (O) contained in oxides, as well as denomination coefficients, it is possible to get the following expression:

$$f_{\text{Si}} = \frac{33,33\text{Si}_{\text{SiO}_2} + 66,67\text{O}_{\text{SiO}_2}}{521,18\text{Me}_{\text{Me}_x\text{O}_y} + 828,82\text{O}_{\text{Me}_x\text{O}_y}}. \quad (2)$$

In this case, it is not possible to define the amount of oxygen in a glass-forming composition, since the numerator and the denominator consist of the sums of component concentration. Negligence of the existence of silicon and other elements in the system gets the relation of oxygen concentration in the numerator and the denominator, i.e. there is no mathematical logic of the expression any more. At first approximation, it is quite possible to define that formula (2) expresses the oxygen ratio introduced into the glass-forming system by SiO_2 oxide in relation to the total amount of oxygen introduced by other components. How does it influence the connectivity?

In the above extract, the f_{Si} parameter is called “a measure of degree of connectivity of a silicon-oxygen backbone”. The structure of substance in its glassy state is unique, since arranged, similar to crystal, and random structural motives are simultaneously present. If tetrahedron $[\text{SiO}_4]$ is the basis of a structure, then various structural motives can be revealed in a siliceous glass-forming substance. It can be confirmed in case of gel (as a model), which was formed during drying the glass-forming alkali-lead-boron-silicate composition synthesized in water for the generation of hydrogen microspheres (Fig. 1) [3, 5-8].

Fig. 1 *a* shows lead silicate crystal nuclei – flat two-dimensional plates in the form of an ellipse, since there were no oval intersection lines typical for rotation bodies and corresponding black-and-white surface images of the neighboring crystals. While the growth substance gets from the mother solution, they folded and condensed having reached a development limit. This minimized the surface area and hence, was energetically worthwhile. Fig. 1 *b-e* shows traces from folding diagonally on fragments of bulk needle crystals. The outer surface of formed crystals has typical traces of folding,

especially in peaky areas of crystals, and traces of thickening in the central part after final overlapping of a plane edge fragment (Fig. 1 *e*). Fig. 1 *b* shows that the substance from the mother solution was introduced into the area of crystallization in a vortexual manner. Moving along the spiral, the flows folded the initial plane and condensed the formed three-dimensional crystal.

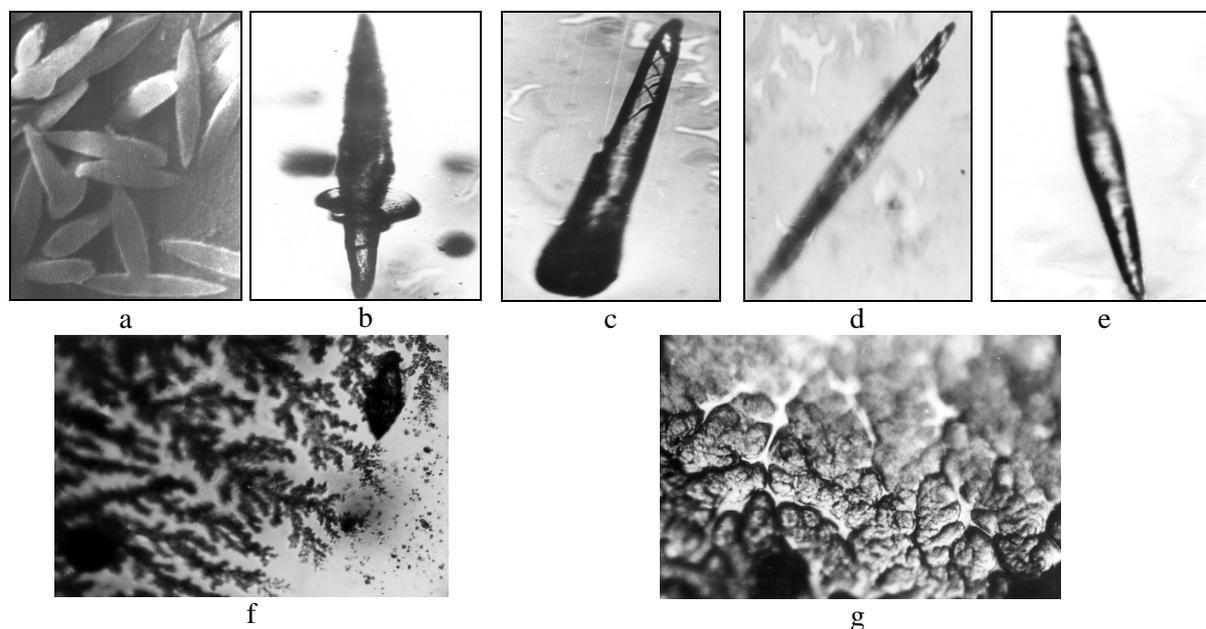


Figure 1. Stages of crystal growth in gel of $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{H}_8\text{C}_6\text{O}_7-\text{H}_2\text{NCSNH}_2$ system: *a* – lamellate crystals, $\times 10^3$; *b* – needle crystals with shadow pattern of mother solution growth substance, $\times 23$; *c-e* – crystals and their fragments with typical traces of two-dimensional structure folding (*c, d* – $\times 23$, *e* – $\times 54$); *f* – dendrite formation centers are available on the right on the free field while growing branches of dendrites are available on the left; *g* – overgrown branches of dendrites at the final stages [6]

During drying, the gel viscosity increased and further development of crystals (“needles”) slowed down. After the bulk of three-dimensional lead silicate crystals was formed, a new crystal phase – dendrites (Fig. 1 *f*) appeared on the surface. In the conditions of retarded introduction of the growth substance from the mother solution to the area of formed phase within the “gel-air” boundary, the one- and two-dimensional crystallization is more energetically favorable than the three-dimensional one. Spot formations (“islands”) were generated at the beginning. Dendrite nuclei settled not chaotically but in a certain sequence, therefore generating dendrite branches as one-dimensional chains. With the growth in two directions, they became flat and consisted of fragments in the form of distorted centers (Fig. 1 *f*, on the upper left).

Dendrites grew in zigzag fashion, which indicated their polymeric structure. While expanding, the dendrite branches were linked with cross bonds, and as a result, the gel surface was completely crystallized (Fig. 1 *g*) – flat structure was formed from one-dimensional fragments.

The image presented in Fig. 1 *f* serves the documentary evidence of the fact that within the structure of glass-forming substance one-dimensional (on the bottom right - islands and chains), flat two-dimensional (on the upper left) and three-dimensional (on the upper right, under dendrites the crystal is captured by vortex streams) crystal motives may exist simultaneously.

It is unclear how the f_{Si} parameter defines the connectivity of all these motives and due to what types of bonds. There is no physical meaning of expression (1).

For the binary $\text{Na}_2\text{O}-\text{SiO}_2$ system, being fundamental for many technological processes, the f_{Si} parameter is nothing but silicate module n_{Si} [7] equal to the relation of SiO_2 and Na_2O oxides

concentration; Na₂O is the oxygen donor during the formation of the silicate glass structural network. Is it reasonable to define one and the same value with various symbols different in their meaning: the silicate module and the measure of connectivity of a silicon-oxygen backbone?

The issue may be studied from the point of view of silicate-crystal chemistry. Infrared spectroscopy justifies the formation of tetrahedrons [AlO₄], [BO₄], [BeO₄], [LiO₄] in natural silicate minerals [9]. It is known that due to their close resemblance, spectral bands of [AlO₄] and [SiO₄] tetrahedrons are almost inseparable from each other. Structures of aluminum, boron and beryllium silicates may have a three-dimensional backbone where tetrahedrons are connected among themselves by oxygen located in peaks. At the same time, island motives, where [SiO₄], [BO₄] and [BeO₄] tetrahedrons are not connected among themselves, are formed (isolated). This is confirmed by the corresponding individual bands in IR spectrums; i.e. aluminum, boron and beryllium form individual structural motives irrespective of silicon and, hence, do not act as donors of oxygen during structurization, on the contrary, similar to silicon they act as oxygen acceptors.

Due to crystallographic similarity [AlO₄], tetrahedrons can replace [SiO₄] tetrahedrons. In such minerals as cyanite, andalusite, sillimanite, mullite, irrespective of [SiO₄] groups, there are [AlO₆] octahedrons. Besides, aluminum forms [AlO₅] discrete groups ("islands"). The structure of andalusite differs in the fact that [SiO₄] groups are isolated from [AlO₆] chains and [AlO₅] "islands". Much the same structure is typical for cyanite.

In the structure of muscovite, every fourth [SiO₄] tetrahedron is replaced with [AlO₄] tetrahedron, where the excess negative charge is compensated by a monovalent cation of Na⁺ or K⁺. It is possible if the structure is formed by silicon and aluminum, and alkaline components act as oxygen donors.

[MgO₄], [FeO₄], [CaO₄], [ZnO₄] tetrahedral groups are also formed in pyroxenes, amphiboles, micas; biotite; α-Ca₂SiO₄; willemites.

In the context of the considered subject, the incompatibility of TiO₂ and ZrO₂ oxides with silicate melts and opacification of glass with P₂O₅ oxide are significant.

For crystal silicates, the sizes (Σ) of some ions [9] are empirically verified: Si⁴⁺ 0.39, Be²⁺ 0.34, P⁵⁺ 0.35, S⁶⁺ 0.34, Ge⁴⁺ 0.44, As⁵⁺ 0.47. These ions are comparable with Si⁴⁺ ions, and the tetrahedrons thus formed can replace [SiO₄] tetrahedrons. Oxygen donation during the formation of the silicate structure is highly improbable; otherwise, polyhedrons with such cations shall differ in their configuration and shall be positioned in voids of a structural network.

The strongest structural polyhedrons are formed by B³⁺, Si⁴⁺, Ge⁴⁺ cations; the field force of cations f_{Kat} (Kl/m²) equals 1200, 380.7, 227.8 respectively. High comparable values of f_{Kat} and bond-breaking energies ΔH_{298}^0 (kcal/mol) B-O 162, Si-O 191.3 and Ge-O 157.5 (for comparison $\Delta H_{298, \text{Na-O}}^0 = 61$ kcal/mol) [10] confirm incorrect formula (1) for f_{Si} calculation. Glass-forming oxides do not act as oxygen donors for SiO₂.

Cations that differ in electrostatic energy (field force) when interacting with oxygen form independent polyhedrons, which are embedded in the structure or voids of a structural network. The segregation process takes place if there are small-size cations with big field force in a glass (radius B³⁺ 0.20 Å [9]). Segregation in the boron silicates is caused by the formation of the boron structure from [BO₃] trigonal groups isolated from the silicate structure with the increase in a Na₂O alkaline component. As a rule, the IR spectrums fix bands typical for SiO₂ oxide and silicates, B₂O₃ oxide and borates. The synthesis of boron silicates in the formation of the B-O-Si bond requires particular technological conditions; their reference spectrums such as X-ray and IR spectrums are not yet available [11].

Phase stratification in the form of liquation was observed during gel formation and subsequent drying of a glass-forming structure within the Na₂O-K₂O-PbO-B₂O₃-SiO₂-H₈C₆O₇-H₂NCSNH₂ system obtained in aqueous media (Fig. 2) [6].

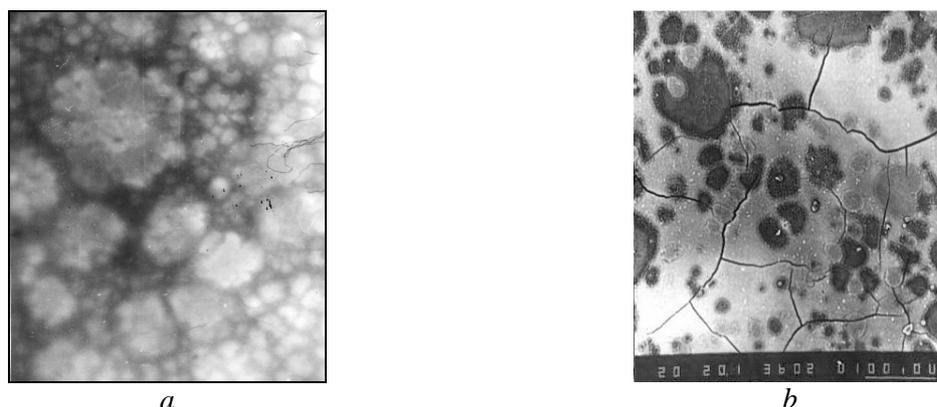


Figure 2. Liquefaction into the $\text{Na}_2\text{O}-\text{K}_2\text{O}-\text{PbO}-\text{B}_2\text{O}_3-\text{SiO}_2-\text{H}_8\text{C}_6\text{O}_7-\text{H}_2\text{NCSNH}_2$ system: *a* – agglomerates of drops in the gel, $\times 23$; *b* – drop structure of xerogel, $\times 200$ [6]

Phase separation, i.e. liquefaction and crystallization of lead silicate (Fig. 1, 2), took place during the drying of alkali-lead-boron-silicate solutions. During water evaporation, the drops were united into large agglomerates (Fig. 2 *a*) – light and dark; lead silicate was concentrated in agglomerates from dark drops; in the central parts of agglomerates, fragments of needle crystals (points that are different by contrast) (Fig. 2 *b*) are observed.

Value f_{Si} calculated by formula (1) for the substance of a specified system makes it impossible to conclude whether the structure is crystallized or amorphous, although several crystal phases and liquefaction (Fig. 1, 2) are revealed.

The f_{Si} and $\mathbf{R}=f_{\text{Si}}^{-1}$ parameters are too formal to estimate the structure of silicates, and they are irrelevant for practical application in glass technology, including sol-gel technology.

The following mathematical expressions for the specified parameters with a different meaning are alternatively suggested.

The mass fraction of oxygen in p_{O} oxide and the amount of O_i oxygen (oxygen number) introduced by the i component with known C_i concentration in glass composition can be calculated by formulas (3) and (4) respectively:

$$p_{\text{O}} = \frac{A_{\text{rel}} N_{\text{O}}}{M_{\text{rel}}}, \quad (3)$$

$$O_i = C_i p_{\text{O},i}, \quad (4)$$

where A_{rel} , M_{rel} – relative (rel) weight of an oxygen atom and an oxide molecule respectively; N_{O} – amount of oxygen atoms in a i -molecule.

Then the total amount of O (5) oxygen in glass can be presented as the sum of oxygen introduced by glass-forming elements (Gf) O_{Gf} , modifiers (Mod) O_{Mod} and intermediate (Int) oxides O_{Int} :

$$O = O_{\text{Gf}} + O_{\text{Mod}} + O_{\text{Int}}. \quad (5)$$

The amount of silicon (Si) in a glass-forming structure is calculated similarly:

$$p_{\text{Si}} = \frac{A_{\text{Si,rel}} N_{\text{Si}}}{M_{\text{SiO}_2, \text{rel}}}, \quad (6)$$

$$\text{Si} = C_{\text{SiO}_2} p_{\text{Si}}, \quad (7)$$

where $A_{\text{Si,rel}}$, $M_{\text{SiO}_2, \text{rel}}$ – relative weight of a silicon atom and a SiO_2 molecule respectively; p_{Si} , N_{Si} – mass fraction and amount of silicon atoms in SiO_2 molecule respectively; C_{SiO_2} – concentration of SiO_2 oxide.

Then, expressions (1) and (2) are transformed as follows:

$$\mathbf{R} = \frac{O_{\text{Gf}} + O_{\text{Mod}} + O_{\text{Int}}}{C_{\text{SiO}_2} p_{\text{Si}}}, \quad (8)$$

$$f_{\text{Si}} = \frac{C_{\text{SiO}_2} p_{\text{Si}}}{O_{\text{Gf}} + O_{\text{Mod}} + O_{\text{Int}}}. \quad (9)$$

Thus, parameter \mathbf{R} (8) is the total amount of oxygen in a glass-forming structure per the number of silicon atoms. There is nothing particular with regard to parameter f_{Si} (9). According to [7], f_{Si} is a measure of “a degree of connectivity of a silicon-oxygen backbone”. Hence, dependence $\mathbf{R}=f_{\text{Si}}^{-1}$ gives rise to doubts.

The function of a connectivity measure of the glass structural network with any component and a set of oxides-glass-forming elements is most likely to be ensured by the connectivity factor of the Y structure suggested by N.N. Ermolenko [2]:

$$Y = \frac{\sum_j I_j Z_j - \sum_k I_k}{\sum_j I_j}. \quad (10)$$

Taking into account the recommendations of the author [2], formula (10) is transformed as follows:

$$Y = \frac{\sum_j x_j C_j Z_j - \sum_k x_k C_k}{\sum_j x_j C_j}, \quad (11)$$

where Z – valence or coordination number; $x_{k(j)}$ – number of metal atoms in oxide molecule; j , k – oxides containing cations with $Z>1$ and $Z=1$ valence respectively; C – oxide content, mol %; $I_{j(k)}=x_{j(k)}C_{j(k)}$.

The sign “–” in the numerator means that alkaline oxides disturb the glass structure. Formula (11) may be applied to forecast the dimension of glass structures: $Y=4$ indicates the formation of a three-dimensional network (an extreme case when $C_{\text{SiO}_2}=100$ mol %), $Y=3$ indicates the formation of a two-dimensional layered structure, $Y=2$ indicates the formation of a one-dimensional chained structure; if $Y<2$, the glass is not formed. The [2] describes the corresponding structural motives. However, the author failed to explain why “ Z ” serves as a valence or a coordination number; they are not equivalent in crystals and even much less in glass obtained from melts of one and the same composition in different conditions. Due to nonequivalence of bonds even in case with elementary substances, it is difficult to define the first coordination shell of the central atom [12].

Table 1. Statistics of multicomponent glass compositions

Oxide X_xO_y	C_i , mol %	O_i , mol %	Range of parameters			
			ΣO_i , mol %	$p_{0,i}$	f_i , Kl/m ²	Y
B ₂ O ₃	1.5–68.3	1–47.1	12405.8	0.7	1200.0	2–395
Li ₂ O	0–2.7	0–1.4	210.3	0.5	44.4	
Na ₂ O	0–44.0	0–2.0	833.1	0.3	17.7	
K ₂ O	0–12.0	0–4.1	56.1	0.2	9.0	
PbO	0–3.8	0–0.3	53.7	0.1	21.9	
Bi ₂ O ₃	0–20.0	0–2.0	65.6	0.1	35.7	
BaO	0–36.0	0–3.6	64.3	0.1	17.6	
Al ₂ O ₃	0–20.0	0–9.4	160.6	0.5	192.0	
ZnO	0–6.4	0–1.3	119.6	0.2	58.4	
La ₂ O ₃	0–17.5	0–2.6	68.8	0.2	59.3	
CaO	0–10.0	0–2.9	274.7	0.3	33.3	
Tl ₂ O	0–40.0	0–1.6	14.2	0.04	7.7	
SiO ₂	0–97.5	0–51.7	5778.2	0.5	380.7	
Rb ₂ O	0–50.7	0–4.6	42.3	0.1	7.3	
CuO	0–30.0	0–6.0	119.0	0.2	50.0	
GeO ₂	0–17.5	0–5.4	600.8	0.3	227.8	
P ₂ O ₅	0–0.3	0–0.2	32.7	0.6	692.0	
MgO	0–5.9	0–2.4	14.6	0.4	75.7	
NiO	0–5.0	0–1.1	5.5	0.2	67.2	
Eu ₂ O ₃	0–0.6	0–0.1	0.1	0.1	37.6	
FeO	0–0.1	0–0.02	0.02	0.2	56.9	
basGf	49.3–99.8	30.9–55.4	5145.5			
addGf	0–20.0	0–9.4	90.6			
Gf	49.3–100	31.1–55.8	5236.1			
basMod	0–50.7	0–11.4	506.0			
addMod	0–40.0	0–6.0	17.3			
Mod	0–50.7	0–11.4	523.3			

Note. basGf, basMod – main glass-forming elements and modifiers accordingly; addGf, addMod – additional glass-forming elements and modifiers accordingly.

Oxygen number O (5) and factor Y (11), are logically related, but definitely not directly (as in [5]) and somewhat differently. Data on 116 multicomponent compositions (poly) containing oxides-glass-forming elements SiO₂, B₂O₃, GeO₂, P₂O₅ (Tab. 1) and on 43 compositions of two-component glasses (bi), including with SiO₂, B₂O₃, GeO₂ oxides (Tab. 2), were selected from literature to provide a strong evidence thereof. As a result of the analysis of oxygen numbers (5) and factors of connectivity (11), the equations for bond Y=f(O) (12), (13) and the relative n_{Gf} (14) module were generated:

$$Y_{\text{poly}} = -0.71 + 0.08O \quad (12)$$

$$Y_{\text{bi}} = 2.22 + 0.01O, \quad (13)$$

$$n_{\text{Gf}} = \frac{C_{\text{Gf}}}{\sum_i C_{\text{Gf},i} + \sum_i C_{\text{Mod},i} + \sum_i C_{\text{Int},i}} = 0,01C_{\text{Gf}}, \quad 0 < n_{\text{Gf}} < 1, \quad (14)$$

where C_{Gf} – concentration of a particular glass-forming element, mol %; $\sum_i C_{Gf,i}$, $\sum_i C_{Mod,i}$, $\sum_i C_{Int,i}$ – sums of concentrations of glass-forming elements, modifiers and intermediate oxides, mol %.

The n_{Gf} module shall be used even if there are no modifiers and (or) intermediate oxides in compositions. Unlike the silicate module, the denominator is nonzero at:

$$\left(\sum_i C_{Mod,i} + \sum_i C_{Int,i} \right) = 0, \text{ and expression (14) is appropriate.}$$

Taking into account the minimum and maximum content of glass-forming elements and oxygen thus introduced in compositions, equation (12) can be used to estimate the connectivity factor of a structure: $Y_{poly, min}=2$, a one-dimensional structure (isle, dendrite structure, Fig. 1 e); $Y_{poly, max}=3.95$, two-dimensional structure with fragments of a three-dimensional structure (almost a three-dimensional structure) similar to the majority of glasses with prevailing content of SiO_2 , as well as to the silica glass.

The connectivity factor of two-component glasses (calculated by formula (13)) varied from 2.6 ($Y_{bi, min}$) to 3 ($Y_{bi, max}$), and the structure changed from one-dimensional with two-dimensional fragments to two-dimensional, which is typical for borate glasses.

Factor Y [2] is more likely to be considered as “a measure of the connectivity degree” of a structure than f_{Si} [5]; it is more universal, which is confirmed by the example of the considered silicate, boron silicate and borate glasses.

Table 2. Statistics for 43 compositions of two-component glasses with B_2O_3

Oxide \mathcal{X}_xO_y	Range of parameters				
	C_i , mol %	O_i , mol %	$p_{O,i}$	f_i , Kl/m ²	Y
B_2O_3	45–100	17.3–69.0	0.7	1200.0	2.6–3
Li_2O	0–12.2	0–6.5	0.5	44.4	
Na_2O	0–15.5	0–4.0	0.3	17.7	
K_2O	0–14.3	0–2.4	0.2	9.0	
Rb_2O	0–16.7	0–1.5	0.1	7.3	
PbO	0–9.4	0–4.9	0.1	21.9	
BaO	0–40.0	0–4.0	0.1	17.6	
MnO	0–50.0	0–11.5	0.2	50.0	
ZnO	0–55.0	0–11.0	0.2	58.4	
CaO	0–50.0	0–14.5	0.3	33.3	
SiO_2	0–20.0	0–10.6	0.5	380.7	
basGf	25–100	17.3–69.0	0.3	227.8	
addGf	0–70	0–11.0			
Gf	25–100	17.3–69.0			
basMod	0–50	0–14.5			
addMod	0–75	0–11.5			
Mod	0–75	0–14.5			

Let us discuss this issue from the standpoint of chemical technology, i.e. synthesis of glass compositions in aqueous media. Compositions are prepared (wt. %, patents of the Russian Federation) for the production of hydrogen microspheres [13] via the drop and frit method [6]: patent 2036171 –

H_3BO_3 8.21–8.31, NaOH 27.60–27.72, KOH 11.01–11.14, Li_2SO_4 0.07–0.70, H_2SiO_3 ; patent 2036856 – H_3BO_3 7.64–7.82, NaOH 26.46–26.72, KOH 10.25–10.8, Li_2CO_3 0.22–0.74, Eu_2O_3 0.7–4.0, $\text{C}_6\text{H}_8\text{O}_7$ 3.9–22.3, $(\text{NH}_2)_2\text{CO}$ 1–3, H_2SiO_3 ; patent 2033978 – H_3BO_3 7.46–7.82, NaOH 25.43–26.59, KOH 10.01–10.36, Li_2CO_3 0.25–0.74, Eu_2O_3 0.7–4.0, $\text{C}_6\text{H}_8\text{O}_7$ 3.9–22.3, $\text{C}_{22}\text{H}_{11}\text{O}_9(\text{NH}_4)_3$.6–3.5, $(\text{NH}_2)_2\text{CO}$ 1.0–2.9, H_2SiO_3 ; patent 2205802 – H_3BO_3 5.56–7.44, NaOH 13.60–15.52, KOH 0.06–0.15, PbO 6.65–6.82, $\text{C}_6\text{H}_8\text{O}_7$ 20.5–22.9, $\text{C}_{22}\text{H}_{11}\text{O}_9(\text{NH}_4)_3$ 0.10–0.24, CaCO_3 5.94–6.06, $\text{Mg}(\text{OH})_2$ 1.17–1.45, $\text{Al}(\text{OH})_3$ 0.02–0.05, H_2SiO_3 ; patent 2235693 – SiO_2 54–60.3, B_2O_3 3.24–7.01, Na_2O 12.31–20.10, K_2O 0.09–1.07, CaO 5.59–6.56, MgO 1.35–2.79, Al_2O_3 0.02–1.13, PbO 11.28–12.53.

Synthesis in aqueous media includes the following. All components were dissolved separately and mixed. Aqueous solution NaOH was used to dissolve silicic and boric acids. Silicic acid was dissolved first with further dissolution of boric acid. Additional components were used in the form of complex compounds [6]. Citric acid and aluminon were used for Mg , Ca , Ag , Pb , Sm , Eu , Ho , Tb ; to receive silicate solution with aluminum – AlCl_3 , aluminon and ammonia; to dissolve Nd_2O_3 – hydrochloric acid and aluminon. Additional gas-forming agent Li_2SO_4 was introduced to prevent collapse of microspheres at 1100–1300°C.

Water was added to samples of silicic and boric acids. Boric acid was completely dissolved, pH was similar to water. Silicic acid did not dissolve in water and hence the pH of its water suspension remained the same. NaOH solution with pH 12 was prepared separately. Silicic acid was dissolved when the NaOH solution was added. The end of synthesis (NaSi) was determined visually until a solid phase of the acid (powder) was completely dissolved and pH of NaSi solution was 12. NaOH and NaSi solutions were applied for the synthesis borate (NaB) and sodium borosilicate (NaBSi) (names are conditional, mixing of such products as silicates, borates, borosilicates was established).

Then, the pH-curves of NaBSi , NaSi , NaB (Fig. 3) were analyzed [14]. S-areas (peaks) due to synthesis of new substances are well defined and divided by horizontal contours. The appearance of three S-areas on NaBSi , NaB curves is caused by three-stage dissociation of H_3BO_3 ($K_1=5\cdot 10^{-10}$, $K_2=1.8\cdot 10^{-13}$, $K_3=3\cdot 10^{-14}$ [15]) and synthesis of sodium mono-, tetra- and pentaborates.

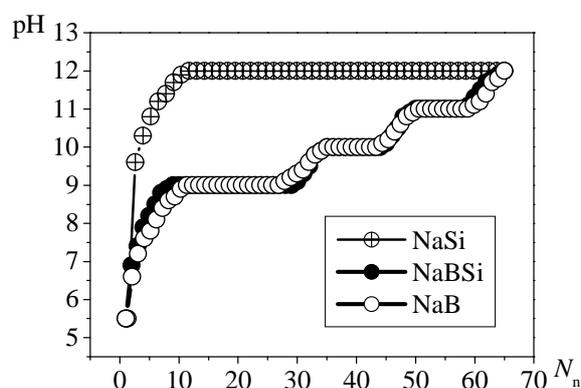


Figure 3. Normalized curves of titration under synthesis: NaSi – sodium silicate; NaB – sodium borate; NaBSi – sodium borosilicate; N_n – normalized amounts of solution aliquots (according to formula (15)) [6]

Horizontal contours with pH uniformity and continuous addition of an alkaline agent indicated the formation of buffer solutions and complex compounds when H_3BO_3 interacted with $\text{B}(\text{OH})_4^-$ anions. The second and third stages are equal lengthwise, but are both shorter than the first one since $K_2 \approx K_3$, but K_2 and K_3 are less than K_1 .

In the alkaline media, H_2SiO_3 dissociates in two stages ($K_1=4.2\cdot 10^{-19}$, $K_2=0.51\cdot 10^{-16}$ [7, 9]), and ions $[(\text{HO})_2\text{SiO}_2(\text{H}_2\text{O})_2]^{2-}$ and $[\text{Na}(\text{H}_2\text{O})_6]^+$ form polymers [7]. When $n_{\text{Si}} < 3$, high-polymer forms are absent [7]. Peaks are almost invisible on the pH curve for NaSi due to high activation energy of chemical interaction between silicic acid and NaOH hydroxide in the solution, the curve shape is attributed to alkali added into the solution. Random pH values (“noise”) were removed via smoothing: the arithmetic mean (smoothed) value was calculated from four successive values. When the stage equaled one, the data were separately analyzed for each synthesis. The example of this procedure is given in Tab. 3. The processes finished at pH 12 (final solution). The difference of curves lengthwise is caused by the different speed of processes. Due to thermodynamic instability (“noises”), the pH values may be considered random. The standard normalization was applied: having selected the corresponding coefficients, the titration curves led to the biggest length (15) (Fig. 3):

$$N_n = N_{\text{norm}} \frac{n_{\text{max}}}{n_{\text{norm}}}, \quad (15)$$

where N_n – normalized value; N_{norm} – normative value; n_{norm} – length of the normative curve equal to the amount of aliquots of the corresponding component (single volume added with a feeder); n_{max} – length of the biggest curve.

It is critical to follow the order of agent mixing during synthesis since phase separation is possible. It is impossible to add sodium hydroxide solution to the mixture of silicic and boric acids being placed in the same reaction vessel. In this case, a larger portion of the alkaline agent was used in synthesis of borate, while silicates were formed on a second-priority basis. In case of alkali shortage, some part of silicic acid remained in a free state.

Table 3. Smoothing of pH experimental values

n_i	pH		n_i	pH	
	measured	smoothed		measured	smoothed
1	2	–	9...	3...	2.6...
2	2	–	62	12	11
3	2	–	63	12	11
4	2	2	64	12	11.1
5	2.5	2.1	65	12	11.2
6	2.5	2.2	66	12	11.5
7	2.5	2.4	67	12	11.8
8	2.5	2.5	68	12	12

Note. n_i – amount of NaOH aliquots added to silicic acid suspension

The inclusion of the additional (excess) alkaline agent led to the change in the quantitative ratio of composition components. This could cause change in glass properties, which is unacceptable in the technology of hydrogen microspheres. It was experimentally proved that boric and silicic acids compete with each other thus interacting with sodium hydroxide in aqueous media. While in silicate solution, the maximum pH value, necessary for the synthesis, was still reached; in borate solution, the interaction of boric acid with sodium hydroxide was already completed. The donor of boric acid during synthesis of silicates is not confirmed. Expression (1) is unjustified for the synthesis of the glass-forming composition in aqueous solution, such as in case with sol-gel technology.

3. Results and discussion

It is impossible to state firmly that such parameters as “a measure of the connectivity degree of a silicon-oxygen backbone” (f_{Si}) and “the oxygen number” (R) reflect adequately the role of oxides in structurization of siliceous glasses. There is no substantiated evidence of the dependence of

connectivity value f_{Si} and number R on the amount of oxygen, and the relation between f_{Si} and R . The results of physical and chemical study prove that the glass structure represents a complex hierarchy of various types of crystal motives, which can exist simultaneously or in various combinations. It is not possible to describe the relation between some parts and the whole – motives and a structure – f_{Si} and R .

4. Conclusions

The following criteria were suggested as an alternative to f_{Si} and R parameters in order to define the role of components in the structure, and hence, properties of glass: p_O – ratio of oxygen in a glass component; O_i – oxygen number; O – total amount of oxygen in glass composition; Y – factor of structure connectivity; n_{Gf} – relative module. The universality of Y and n_{Gf} criteria is caused by the fact that they consider every single component of glass compositions. Alternative criteria are logical and easy to calculate. Functional dependence of $Y=f(O)$ was established within two- and multicomponent structures with SiO_2 , B_2O_3 , GeO_2 , P_2O_5 oxides to forecast types of formed structures. The results of the forecast do not contradict any known factual evidence.

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