BAZICITATEA BIOSTICLELOR SILICATICE
BASICITY OF SILICATE BIOGLASSES

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Biomaterials, which are increasingly used in the field of restorative medicine, may represent vitreous, glass-ceramic or ceramic systems, all of which have one common feature: bioactivity. The acid-basic character of the interactions at the interface organic material - inorganic material (implant) determines the acceptance speed and life duration of the implant.

As a result, there is a strong correlation between basicity and bioactivity, which must be expressed quantitatively. Therefore, in this paper it is emphasized that the bioactivity of silicate glasses is closely correlated with the basicity percentage, pB.

Based upon a mathematical model of optimal programming, the limits of pB were determined, between which the biocompatibility for the glasses from the complex silicate systems highlighted: pB = 60 ÷ 70%, a result compared and confirmed by a series of data from specialized literature.

Biomaterialele, utilizate din ce în ce mai mult în domeniul medicinii reparatorie, pot reprezenta sisteme vitroase, vitroceramice sau ceramice, toate având o caracteristică comună: bioactivitatea. Caracterul acido-bazic al interacţiilor la interfaţa material organic – material anorganic (implant) determină viteza de acceptare şi durata de viaţă a implantului.

Rezultă că între bazicitate şi bioactivitate există o corelaţie puternică, care trebuie exprimată cantitativ. De aceea, în această lucrare se evidenţiază faptul că bioactivitatea sticlelor silicatice este strâns corelată cu ponderea bazicităţii, pB, a acestora.

Pe baza unui model matematic de programare optimală s-au determinat limitele de pB între care se evidenţiază biocompatibilitatea pentru sticlele din sistemele silicatice polinare (complexe) : pB = 60 ÷ 70%, rezultat comparat şi confirmat de o serie de date din literatura de specialitate.

Keywords: *silicate bioglass, basicity, oxide composition – basicity - bioactivity*

1. Introduction

Biomaterials began to be used in the field of restorative medicine in the 1960s. These were systematically synthesized and characterized starting with the publication of the results of Hench et al. [1]. Depending on their oxide composition and the particularities of the genesis route, biomaterials may have the most diverse applications.

From the point of view of the chemical structure, the biomaterials can represent vitreous, vitroceramic or ceramic systems, all having a common characteristic: the bioactivity [2-8]. The paper shows that the bioactivity of silicate glasses is closely correlated with the amount of their basicity.

2. Theoretical background

The bioactivity of the oxide materials represents their ability to develop at the interface organic material - inorganic material (implant) a layer of hydroxyapatite that can be integrated into the living tissue. This process is basically a chemical reaction between oxides. The redox reaction involves an electron transfer between the oxygen atoms of the participating oxides. As a result, their acid-base character matters and determines the rate with which they are performed and the duration of implanting, as shown by the data presented in Figure 1 [1]. From here, a logical consequence is that between basicity and bioactivity there is a strong correlation, which must be transformed from the qualitative register into a quantitative one.

2.1. Evaluation of the basicity of oxide glasses

Establishing the content of acid-base terms has always been a challenge for chemists. On this subject, the different approaches are briefly presented in the papers [9,10].

From the point of view of the quantitative evaluation of the oxide basicity, two parameters were imposed, proposed by Duffy et al. at the level of the '70s and, respectively, Balta et al. in the ‘80s. These are: **optical basicity, Λ,** and, respectively, **the basicity percentage, pB**, **in %.** Both parameters can be calculated with additive relationships for glasses with complex chemical composition, but can also be determined experimentally, spectroscopically (see details in

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papers [9,10]). Although they have completely different starting hypotheses, the values obtained through the two approaches are numerically correlated through a simple transformation relation.

In the paper it was preferred to use, for oxide systems, the structural parameter pB because it is defined on a natural scale of basicity, which has as reference value (100%) the O^{2-} ion. For an oxide, pB is calculated with the relation proposed by Balta and Radu:

$$\lg pB = 1{,}9 \cdot (CN)^{0{,}02} - 0{,}023 \cdot \frac{P_i}{CN} \qquad (1)$$

where ***CN*** is the coordination number of the cation M^{z+} related to oxygen to oxygen; P_i = ionization potential for the oxidation state z^+ of the corresponding cation, in eV;

For complex oxide glasses pB is calculated with the relation:

$$pB = \sum_{i=1}^{n} pB_i \cdot c_i \qquad (2)$$

where pB_i is the basicity of oxide *i* ; c_i – the gravimetric fraction of oxide *i* ; *n* – the number of oxides components of the glass.

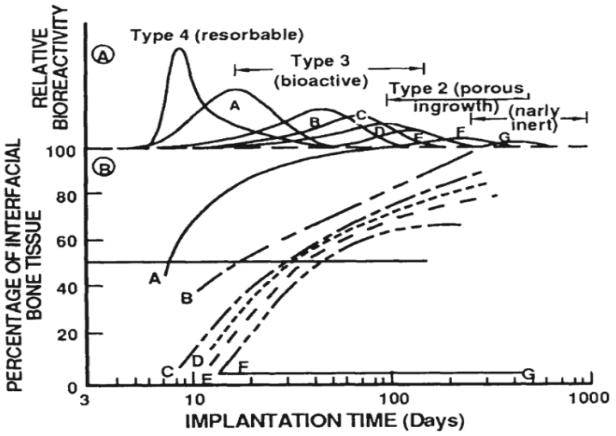

Fig. 1 – Bioactivity spectrum for various implants: (A) Relative rate of bioactivity; (B) Time dependence of formation of bone bonding at implant interface / *Spectre de bioactivitate pentru diverse implanturi: (A) Viteza relativă a bioactivităţii; (B) Dependența de timp a formării legăturii cu osul la interfața implantului.*
A – 45S5 Bioglass; **B** – KGS Ceravital; **C** – 55S4.3 Bioglass; **D** – A/W Glass-ceramic; **E** – HA; **F** – KGX Ceravital; **G** – Al_2O_3–Si_3N_4 [1]

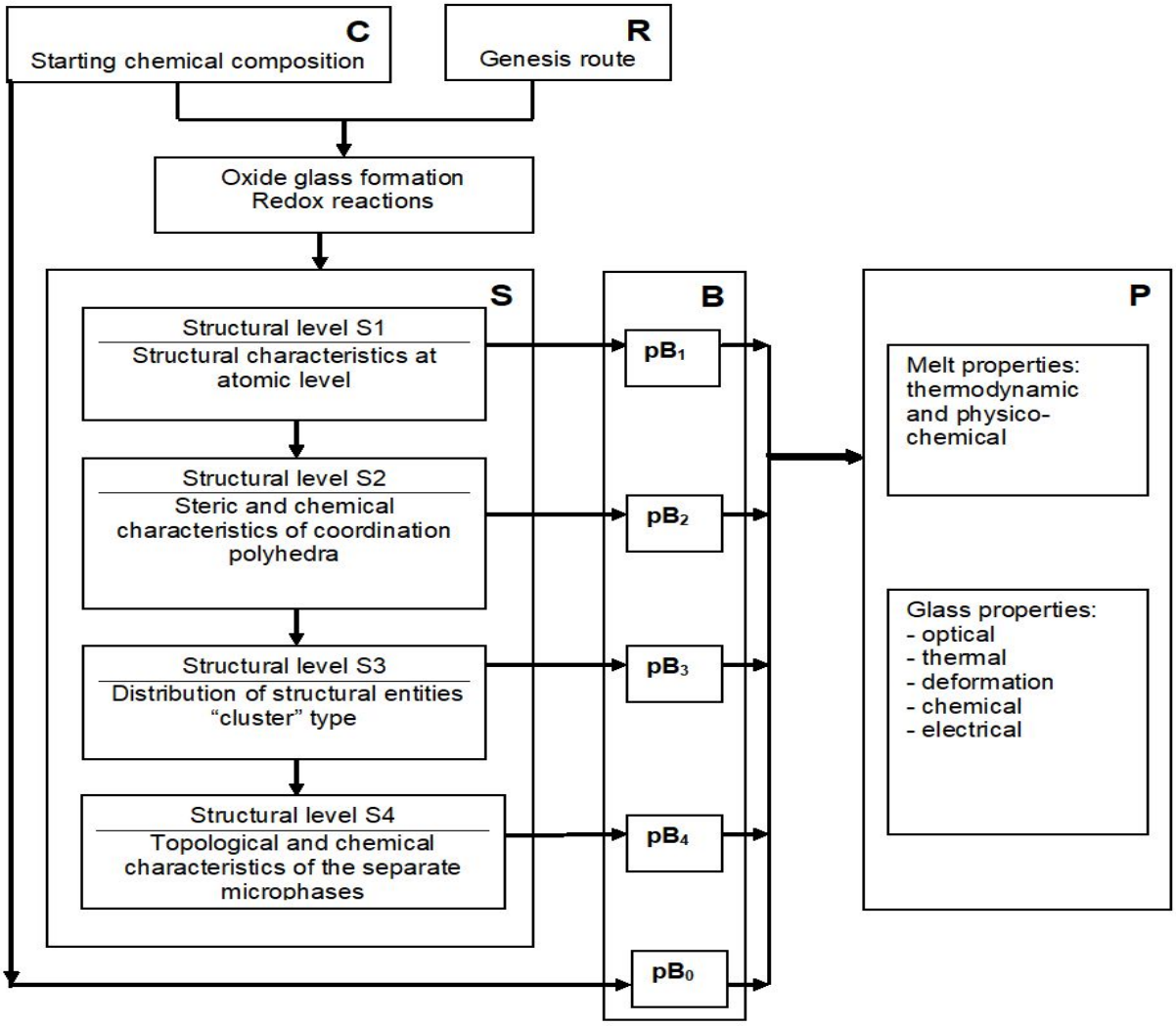

Fig. 2 – Correlations oxide composition ***C*** → genesis route ***R*** → structure ***S*** → basicity ***B*** → properties ***P*** in vitreous oxide systems / *Corelații compoziție oxidică **C** → rută de geneză **R** → structură **S** → bazicitate **B** → proprietăți **P** la sistemele oxidice vitroase.*

Table 1

Relationships between the basicity pB of the oxide glasses and a series of chemical-structural characteristics at various levels
*Relații între bazicitatea **pB** a sticlelor oxidice și o serie de caracteristici chimico-structurale la diverse niveluri [9,11].*

Structu-ral level	Types of chemical-structural entities according to the structural level	Dependency relationship	Remarks
S1	Electronegativity Gorgy, x_G	$x_G = 2.9636 - 0.0232 \cdot pB_1$	12 oxides [9]
	The intensity of the electrostatic field, Z/a^2	$Z/a^2 = 3.1452 - 0.0330 \cdot pB_1$	12 oxides [9]
	Polarizability of the oxygen ion, $\alpha_{O^{2-}}$	$1/\alpha_{O^{2-}} = 1.1560 - 0.0090 \cdot pB_1$	12 oxides [9]
	The bonding energy O^{1s}, E_b	$E_b = -0.092 \cdot pB_1 + 536.76$	29 oxides [9]
	Bonding ionicity according to the dielectric theory, f_i	$pB_1 = 0.3445 \cdot f_i + 53.026$	10 oxides [9]
	The cation bonding energy in oxides, E_B^c	$E_B^c = 0.0771 \cdot pB_1^2 - 12.844 \cdot pB_1 + 549.63$	29 oxides [9]
	Optical basicity, Λ	$\Lambda = 0.0181 \cdot pB_1 - 0.3634$	29 oxides [9]
	Basicity percentage, ***pB***	Relation (1)	All oxides [11]
S2	Coordination polyhedra of cations of network formers oxides, Q^n $Q^n \equiv Si(Q_b)^n \cdot (Q_{nb})^{4-n}$; $n = \overline{0,4}$;	$pB_2 = \sum_{n=0}^{4} c_{2n} \cdot pB(Q^n)$ c_{2n} – polyhedron concentration Q^n	Alcalino-silicates glasses [11]
S3	Distribution “clusters” Ex.: $C_x = xSiO_2 \cdot (2x - fx)Na_2O$	$pB_3 = \sum_{x=1}^{x_{max}} c_x \cdot pB(C_x)$ c_x - molar / gravimetric fraction for cluster type x	Alcalino-silicates glasses [11]
S4	The basicity percentage $pB_4^{'}$, $pB_4^{''}$ and ***f'***, respectively, ***f''*** the molar (or gravimetric) fractions of the two phases	$pB_4 = pB_4^{'} \cdot f^{'} + pB_4^{''} \cdot f^{''}$	All oxide glasses with separate microphases [11]
--	Oxide composition, oxide basicity, B_i	$pB_0 = \sum_{i=1}^{n} c_i \cdot B_i$, $\sum_{i=1}^{n} c_i = 1$	All oxide glasses [11]

Remake: The dependence relations between basicity and different structural properties at different levels are characterized by correlation coefficients R_c^2 over 0.900 / *Relaţiile de dependență dintre bazicitate și diferite proprietăți structurale la diverse niveluri sunt caracterizate de coeficienți de corelație R_c^2 peste 0.900.*

As shown in relation (1), the basicity percentage is defined according to a series of characteristics of the cations of the component oxides. In addition, pB could be placed in quantitative dependencies with a number of other chemical-structural parameters [9,10].

As such, the evaluation of the basicity of the oxides by means of pB allowed to highlight its influence on some thermodynamic properties of the oxide melts [11-13], but also on some properties of the rigid glasses [9,10]. In summary, the main interactions between the components of the triad: structure – basicity – properties, are presented in Figure 2 and in the Table 1 [9,11].

As expected, the basicity percentage of the oxide systems determines their ability to be obtained in a vitreous state. In summary, in this context, the main ideas presented in the paper [14] are:

- The ability to obtain oxide glasses by undercooling some melts increases when the **pB** for them decreases from **60% to 40%** respectively, varies **from 70% to 60%**; on the same domains of pB, but in the opposite direction, the tendency to crystallize melts at undercooling varies, respectively, "critical cooling rate", CCR [15];
- **The basicity percentage about 60%** delimits the glass-ceramic oxide systems that are obtained by homogeneous surface crystallization (**pB > 60%**) compared to those with heterogeneous crystallization, which require the addition of nucleators (**pB < 60%**) [9,11];
- In Doremus' methodology [16], the **”strong”** oxide glasses are characterized by **pB < 60%**, while the **”fragile”** glasses have **pB > 60%;**
- In general, oxides with **pB < 60%**, can form glasses by undercooling (they are **network formers**); those with **pB > 70%** are **network modifiers** and can be obtained as glasses by

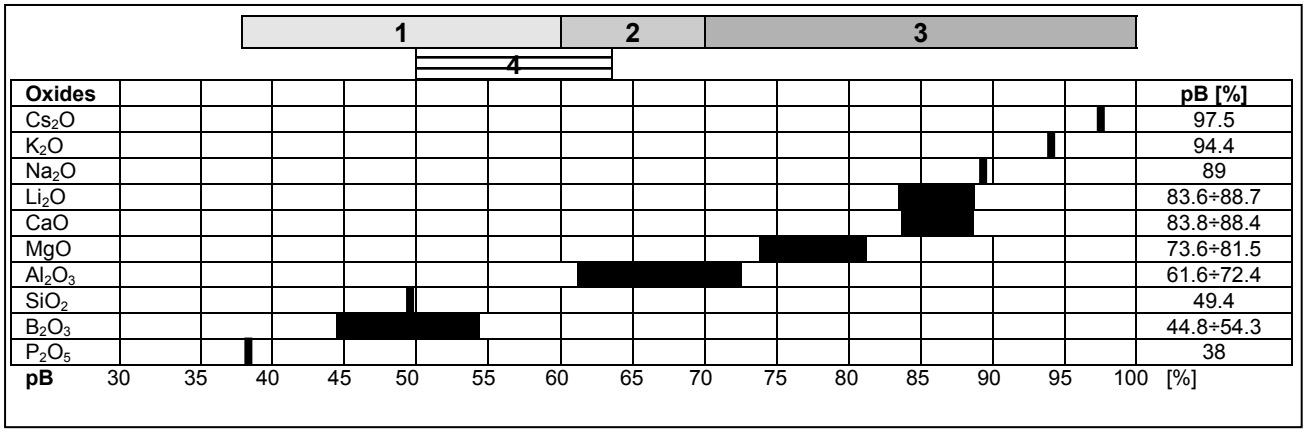

Fig. 3 – Basicity percentage for various oxides present in the vitreous systems: 1 – formers; 2 – intermediates; 3 – modifiers; 4 – industrial glasses (some oxides have variable values of pB because depending on the chemical composition, they have different coordination numbers). / *Ponderea bazicității pentru diverse clase de oxizi prezenți în sistemele vitroase: 1 – formatori; 2 – intermediari; 3 – modificatori; 4 – sticle industriale (unii oxizi au valori variabile de pB deoarece, în funcție de compoziția chimică, prezintă numere de coordinare diferite).*

means of unconventional ultra-fast cooling techniques; oxides with **pB = 60 ÷ 70%** represent **intermediate oxides** (see Figure 3) [3,9-14].

As a partial conclusion, it can be considered that the basicity percentage, pB, represents a complex chemical-structural indicator that can be used in both qualitative and quantitative evaluations in relation to the properties of the glasses in general and the bioglasses in particular.

2.2. Optimal design of the oxide composition of bioglasses

The design of materials consists in establishing, based on a mathematical model, their chemical composition, so that a series of specific technological conditions are met. Over time, obtaining more precise relations between property - oxide composition for glasses have been developed for two reasons:

- The creation of more and more extensive databases concerning the composition and properties of vitreous systems of a great variety of composition, interesting for various applications [17,18];
- The use of "classical" mathematical methods (mathematical regression), or relatively recent (method of planning experiments, mathematical programming) or "exotic" (genetic algorithm method and method of artificial neural networks), see, for example, presentations and applications in [14,19-24].

The confluence of the two directions of development of science and technology of oxide materials (but not only) has determinate in obtaining some glass compositions by solving simple mathematical models, initially represented by systems of equations / inequations. They accumulated technological relationships and restrictions regarding the design and processing of glasses [24].

When a performance function is attached to the constraint block, the design model of an oxide material becomes optimal [23,24].

An optimal design model for a bioactive oxide material is composed of:

- A block of constraints represented by a system of linear and/or nonlinear relations, which mathematically models technological (processing) and usage requirements, restrictions imposed on the component oxides and the properties considered;
- The non-negativity condition of the variables;
- An objective (purpose) function group. Usually, this is a leading function, important for the glass developed in relation to the predicted field of use. It is to be optimized, by minimization or maximization, in relation to the pursued purpose [23,24].

Thus, if the mathematical model has a solution and is correctly realized, it provides, from several possible oxide compositions, the one that determines the optimal value of the leading property (the objective function).

Starting from the initial oxide system, analyzed by Hench, SiO_2 – P_2O_5 – CaO – MgO, over time other complex multicomponent systems have been studied, in order to improve various properties of biomaterials (bioglasses) according to their field of use.

Such a system is SiO_2 – P_2O_5 – CaO – Na_2O. For this system the problem was to determine the admissible range of variation of the basicity of the obtained bioglasses using as a method of analysis the mathematical modeling, based upon nonlinear programming.

3. Results and discussion

Based upon the literature information [4,5], for the studied silicate system, the composition of the oxides may vary between certain limits: SiO_2 = 40 ÷ 60%; P_2O_5 = 0 ÷ 8%; Al_2O_3 = 0 ÷ 2%; CaO = 10 ÷ 30%; Na_2O = 20 ÷ 30% (% wt.).

In the paper [4] a parameter is statistically defined that can evaluate the intensity of the bioactivity of the glasses by means of an indicator called "reaction number", ***RN***. It is calculated with the relation:

$$RN = 88.3875 - 0.01163 \cdot (\%SiO_2)^2 - 1.21 \cdot (\%P_2O_5) - \\ - 2.087 \cdot (\%Al_2O_3) - 1.123 \cdot (\%CaO) - 0.98 \cdot (\%Na_2O) \quad (3)$$

The ***RN*** indicator has values between 1 and 7. The recommended range in the case of optimum bioglasses design is ***RN*** = 5 ÷ 7.

The purpose function is represented by the basicity pB, for which the permissible range of variation ($pB_{minimum}$, $pB_{maximum}$) must be determined so that the silicate glasses in the oxide system studied have bioactivity.

If the notations $\%SiO_2$ = **x1**; $\%P_2O_5$ = **x2**; $\%Al_2O_3$ = **x3**; %CaO = **x4**; $\%Na_2O$ = **x5**, are used, the technological conditions presented lead to the following simple mathematical model:

$$\begin{aligned} &40 \le x1 \le 60 \\ &0 \le x2 \le 8 \\ &0 \le x3 \le 2 \\ &10 \le x4 \le 30 \\ &20 \le x5 \le 30 \\ &xi \ge 0 \; ; \; i = \overline{1,5} \end{aligned} \quad (4)$$

$$(opt)pB = (\min/\max)(0.494 \cdot x1 + 0.38 \cdot x2 + 0.616 \cdot x3 + 0.8638 \cdot x4 + 0.89 \cdot x5)$$

Note: In various concrete cases, the model can be supplemented with a series of additional relations representing some properties of interest: the glass transition temperature, viscosity, coefficient of thermal expansion [3÷5].

- ✓ **By solving the programming model (4) the values for $pB_{minimum}$ = 60.6% and $pB_{maximum}$ = 71.2% resulted for basicity**. This result is also supported by a series of data reported in the literature, as follows.
- ✓ Balta, quoted in [11,14], analyzing the oxide compositions for **25 biomaterials** covering classes A ÷ F (see figure 1), established that 22 of them had **pB values of at least 62%**. The maximum values, from the presented graph, **approach pB = 70%.**
- ✓ In the case of the hip prosthesis, the implants need to bear important loads. The solution consists of coating biocompatible metallic materials (Ti, some special alloys) with biocompatible and bioactive glass-ceramic layers. The paper [9] presents a mathematical programming model of a bioglass-ceramic material of interest having the chemical composition placed in the multicomponent oxide system $SiO_2 – B_2O_3 – P_2O_5 – CaO – MgO – Li_2O – Na_2O – K_2O – TiO_2$. The solution of the model led to the determination of the optimum oxide composition for the material that was obtained and tested in the laboratory. **The biomaterial, with a pB value of 62%, has responded well to biocompatibility and bioactivity tests.**
- ✓ In the paper [5], the oxide compositions are presented and synthesized a number of 15 bioglasses, together with the glass transition temperature, Tg (see Table 2).

Table 2

Oxide composition and glass transition temperature Tg for the studied glasses

Compoziția oxidică și temperatura tranziției vitroase Tg pentru sticlelor studiate

Glass code	SiO_2 [%]	P_2O_5 [%]	Na_2O [%]	CaO [%]	B_2O_3 [%]	K_2O [%]	MgO [%]	Tg [°C]
1	70	0	10	15	0	5	0	570
2	68	0	15	15	0	0	2	557
3	67	3	0	10	0	15	5	652
4	64	3	10	15	3	5	0	565
5	59	6	5	15	3	10	2	581
6	59	3	10	15	3	5	5	550
7	55	0	20	10	0	10	5	444
8	52	3	20	10	3	10	2	449
9	52	0	20	10	3	10	5	441
10	52	3	25	10	3	5	2	447
11	50	0	15	15	3	15	2	464
12	42	3	20	20	0	10	5	435
13	42	6	25	20	0	5	2	443
14	39	6	20	20	0	10	5	422
15	39	6	15	20	3	15	2	453

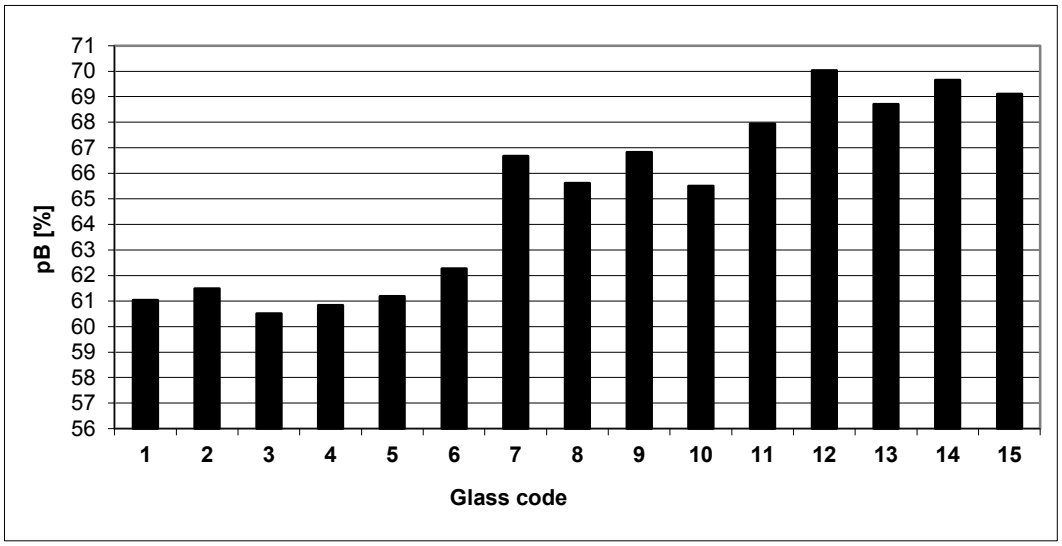

Fig 4 – The pB values for the studied glasses / *Valorile de pB pentru sticlele studiate.*

Table 3

The molar formula of the studied glasses, the ratio ***R*** and **pf**

Formula molară a sticlelor studiate, raportul ***R*** *și* **pf** (R = O / (Si+P+B)) (pf =% SiO_2 +% P_2O_5 +% B_2O_3 (% wt.))

Glass code	SiO_2 [%]	P_2O_5 [%]	Na_2O [%]	CaO [%]	B_2O_3 [%]	K_2O [%]	MgO [%]	*R*	pf [%]
1	1.17	0.00	0.11	0.24	0.00	0.12	0.00	2.405	70
2	1.13	0.00	0.16	0.24	0.00	0.00	0.04	2.385	68
3	1.12	0.03	0.00	0.16	0.00	0.37	0.09	2.555	70
4	1.07	0.03	0.11	0.24	0.04	0.12	0.00	2.378	70
5	0.98	0.05	0.05	0.24	0.04	0.25	0.04	2.501	68
6	0.98	0.03	0.11	0.24	0.04	0.12	0.09	2.485	65
7	0.92	0.00	0.21	0.16	0.00	0.25	0.09	2.776	55
8	0.87	0.03	0.21	0.16	0.04	0.25	0.04	2.637	58
9	0.87	0.00	0.21	0.16	0.04	0.25	0.09	2.701	55
10	0.87	0.03	0.27	0.16	0.04	0.12	0.04	2.574	58
11	0.83	0.00	0.16	0.24	0.04	0.37	0.04	2.833	53
12	0.70	0.03	0.21	0.32	0.00	0.25	0.09	3.192	45
13	0.70	0.05	0.27	0.32	0.00	0.12	0.04	2.992	48
14	0.65	0.05	0.21	0.32	0.00	0.25	0.09	3.221	45
15	0.65	0.05	0.16	0.32	0.04	0.37	0.04	3.066	48

On this basis, and considering the data in Figure 3, it is presented in Figure 4, in the form of histograms, the basicity percentage, pB, for the 15 studied glasses.

Table 3 presents the composition of the glasses calculated in the number of moles, which allowed the determination of the structural parameter ***R***, introduced by Stevels: ***R*** = the total number of oxygen / the total number of cations in the network forming oxides, that is ***R* = O / (Si + P + B)**. If **pf** is noted as the percentage of network forming oxides, **pf = %SiO_2 + %P_2O_5 + %B_2O_3** (% wt.) the analysis of the data from tables 2 and 3 leads to the following conclusions:

- The basicity of the synthesized bioglasses is placed in the following domain pB = 60.6 ÷ 70.0%;
- The values calculated for **pf**, highlight the existence of two groups, characterized by the following values: **pf = 65 ÷ 70%; pB = 60.5 ÷ 62.3%; *R* = 2.38 ÷ 2.55**, respectively: **pf = 48÷ 55%; pB = 65.3 ÷ 70%; *R* = 2.56 ÷ 3.20.**

For the first 6 glasses, characterized by lower values of pB, it seems that pB does not vary significantly with ***R*** (possibly due to the close values for ***R***, which indicates minor structural differences). Next, as the values of ***R*** increase and the pB of the glasses is higher (see Figure 5).

In the context, the increase of the values for **pf** causes a decrease of pB (the formers oxides are more acid oxides), according to the graph in Figure 6. In the opposite direction, the dependence between Tg and **pf** is shown in Figure 7. This result is also confirmed by the graph **Tg versus pB** shown in Figure 8.

The result can be explained by the fact that at small pB the structure of the glasses is characterized by a higher degree of polymerization, higher bonding energies, therefore higher Tg values. In the basic field, the bonding energies and the degree of polymerization of the structure are lower, so Tg takes lower values.

It should be noted that indifferent of the approach of the bioactivity versus basicity relation for silicate glasses having different

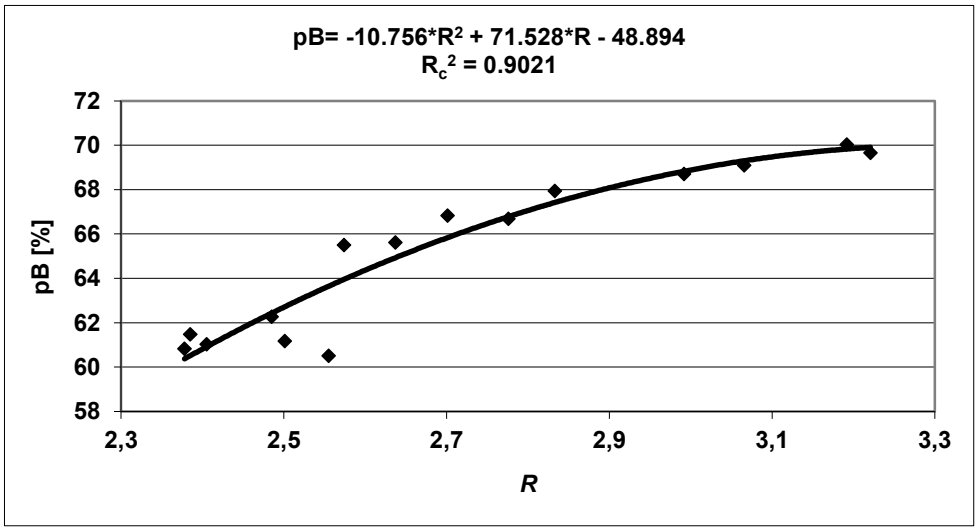

Fig 5 – Variation pB with structural parameter ***R*** / *Variaţia pB cu parametru structural* ***R.***

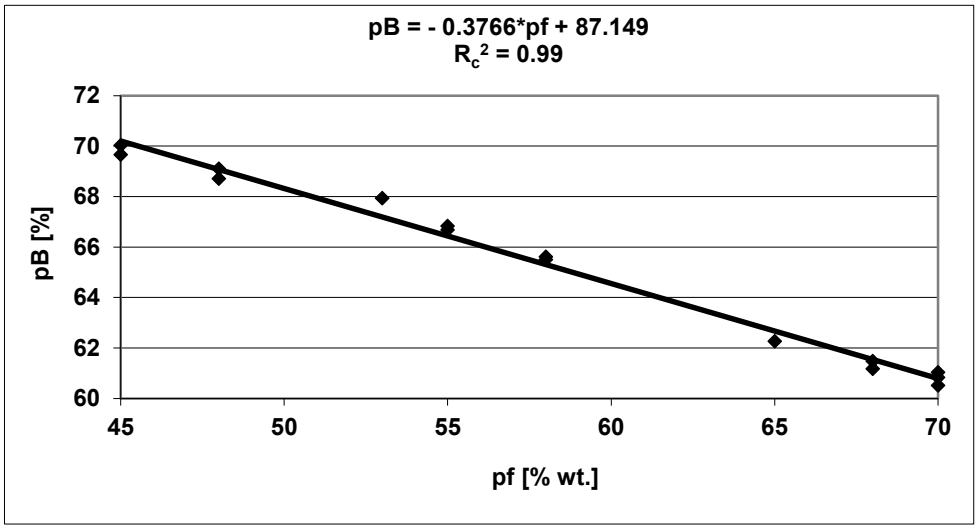

Fig 6 – Variation of pB with the percentage of network formers oxides, **pf** / *Variaţia pB cu procentul de oxizi formatori de rețea,* **pf.**

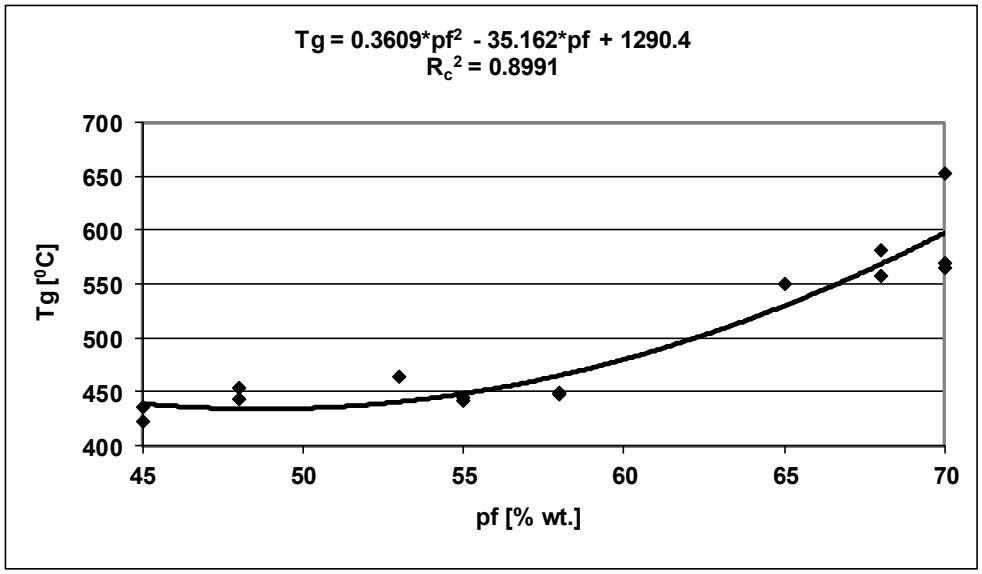

Fig. 7 – Tg versus the percentage of network formers oxides, **pf** */ Tg versus procentul de oxizi formatori de rețea,* **pf.**

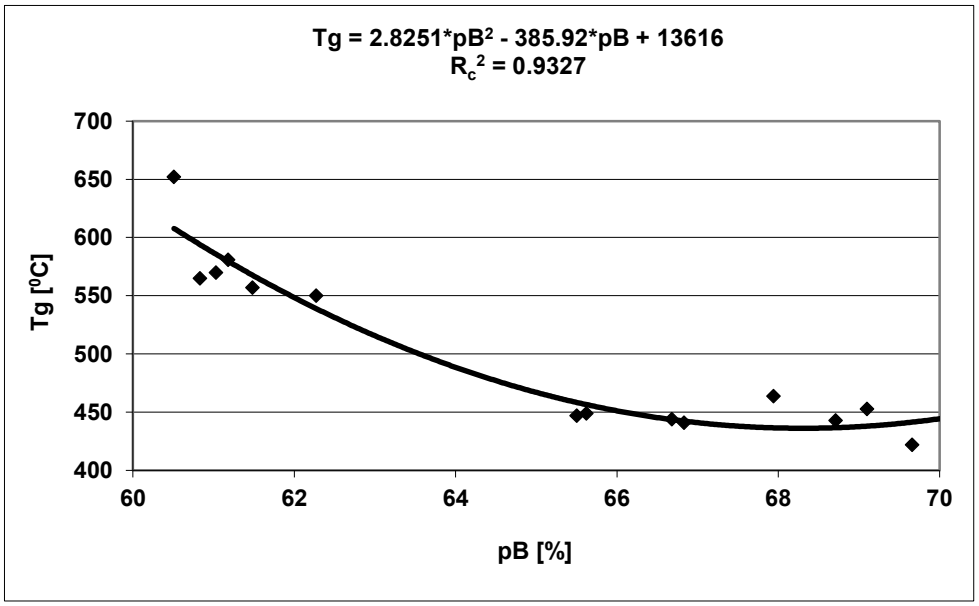

Fig 8 – The variation Tg with the basicity percentage, pB / *Variaţia Tg cu ponderea bazicității, pB.*

Table 4

Chemical-structural characteristics in the Na_2O – SiO_2 system / *Caracteristici chimico-structurale în sistemul Na_2O – SiO_2*

% mol Na_2O	The molar formula of the glass	Crystalline network type / Entity type	x_M	ΔS^{V-C} [J/mol.K]	***R*** // O_b	pB [%]	Type of oxide system
0.0	SiO_2	Three-dimensional network, 3D / Q^4	1	4.22	2 // 4.0	49.4	
25.0	$Na_2O.3SiO_2$	Mixed network / $Q^4 + Q^3$	363	14.57	2.33 // 3.33	59.6	
30.0	$3Na_2O.7SiO_2$	Mixed network / $Q^3 + Q^4$	129	---	2.43 // 3.17	61.7	
33.3	$Na_2O.2SiO_2$	Surfaces, 2D / Q^3	73	14.17	2.50 // 3.0	62.5	
50.0	$Na_2O.SiO_2$	Chains, 1D / Q^2	34	9.14	3.0 // 2.0	69.2	
60.0	$3Na_2O.2SiO_2$	Dimers / Q^1	2	---	3.5 // 1.0	73.2	
66.6	$2Na_2O.SiO_2$	Monomer / Q^0	1	---	4.0 // 0.0	75.9	

- crystallin system - vitreous system - bioglass

Observation: $Q^n \equiv Si(Q_b)^n \cdot (Q_{nb})^{4-n}$; $n = \overline{0,4}$;

oxide compositions, it seems that the range of values 60 to 70% for pB is typical for these classes of vitreous materials. At the same time, it is expected that this acceptable range for pB will correspond to certain intervals for the oxide composition and, implicitly, some associated structural particularities of the vitreous oxide systems.

Because such an analysis for multicomponent oxide systems is practically impossible, two simplifying hypotheses are considered:

- The vitreous silicate systems can be considered, by extrapolation, two-component: SiO_2 (other network formers oxides are present in much smaller percentages compared to SiO_2 or can be evaluated in percentages equivalent to SiO_2) + Na_2O (basic component);
- For such a glass system, the binary system Na_2O – SiO_2 can be considered a "chemical-structural model" having structural equivalences for glasses having the same percentage of SiO_2.

Following this type of approach, Table 4 presents a series of structural characteristics typical of the Na_2O – SiO_2 system depending on the oxide composition.

Crystalline network type / Entity type = Structural topography, N-dimensional / Elementary structural entity type, $\boldsymbol{Q^n}$; x_M – the maximum number of structural entities of type "clusters", present in glasses with a percentage > 0.01% wt.; in glasses the $\boldsymbol{Q^n}$ structural entities have a distribution on the range $Q^0 \div Q^4$ for alkaline oxide compositions > 20% mol .; $\Delta S^{V\text{-}C}$ = the difference of entropy between the vitreous system – the crystalline system of the same composition; O_b = ($O_{nb} = 2\boldsymbol{R} - 4$); $pB = 89 - 40/(\boldsymbol{R}-1)$.

This results in:

- A three-dimensional network is typical for SiO_2, characterized by a minimum value of $\boldsymbol{R}$ ($\boldsymbol{R}$ = 2) and maximum for O_b (O_b = 4). Minimum values for $\Delta S^{V\text{-}C}$ and pB are recorded;
- The addition of Na_2O in the system causes a depolymerization of the SiO_2 network, which tends to be replaced by a distribution of "clusters" of different types. In the beginning there is an increase of x_M – accompanied by the increase of $\Delta S^{V\text{-}C}$, after which x_M begins to decrease. Consequently, $\Delta S^{V\text{-}C}$ and O_b begin to decrease, but $\boldsymbol{R}$ and pB increase. After the composition of the metasilicate, going towards the orthosilicate, no more glasses are obtained by undercooling the melts;
- At higher values of pB, x_M decreases, $\boldsymbol{R}$ increases, and O_b decreases. These melts show an increased tendency to (homogeneous) crystallization. Consequently, the critical cooling rates must increase again, after pB values $\approx$ 70%;
- The glasses in the domain SiO_2 – $Na_2O.SiO_2$ gradually change from the "strong" to the "fragile" character, and Tg decreases. The decrease is made with a higher rate in the range of pB = 60 ÷ 62%, when the structural changes are more significant (mainly bridge break Si – O – Si, possibly P – O – P, B – O – B, B – O – Si etc.). In the more basic field, pB = 65 ÷ 70%, the structural changes are less drastic and, consequently, Tg changes to a lesser extent.

The bioglasses fall within the basicity range 60 ÷ 70%, outside this range they are difficult to obtain.

In the last columns of Table 4, different compositional fields are recorded to obtain typical structures. It turns out that **in order to obtain bioglasses the oxide composition is placed in the trisilicate - metasilicate field, with R = 2.3 ÷ 3.0 and pB = 60 ÷ 70%.**

4. Conclusions

- The basicity percentage, pB, is an integrative chemical and structural indicator that can be used successfully to evaluate the basicity of the oxide systems;
- In a natural way, the bioactivity of silicate bioglasses correlates with their basicity measured by pB. Based on a mathematical model of optimal programming, the limits of pB were determined, between which the biocompatibility for the glasses from the complex silicate systems is highlighted: pB = 60 ÷ 70%;
- The result is compared and confirmed by a series of data from the specialized literature;
- Comparative structural analysis with the "control glasses" in the Na_2O – SiO_2 system for experimental silicate glasses indicated that the ratio $\boldsymbol{R}$ = O / (Si+P+B), the admissible range of variation for pB, as well as the limit oxide compositions are placed in the field of trisilicate - sodium metasilicate.

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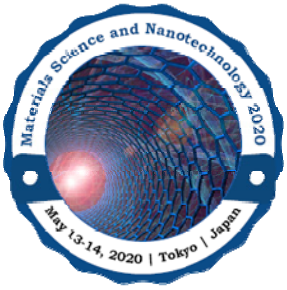

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