

IN MEMORIAM Prof. Dr. Ing. PETRU BALȚĂ

PARTICULARITĂȚI STRUCTURALE ALE STICLELOR DE COMPOZIȚIE $(35-x)\text{Na}_2\text{O}\cdot x\text{Al}_2\text{O}_3\cdot 65\text{B}_2\text{O}_3$ STRUCTURAL PARTICULARITIES OF $(35-x)\text{Na}_2\text{O}\cdot x\text{Al}_2\text{O}_3\cdot 65\text{B}_2\text{O}_3$ GLASS

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In order to better understand oxide glass systems, one approach is based on the composition-structure-properties triad.

In the present article, a series of glasses, belonging to the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ has been analyzed. For this analyze, data determined by authors, presented in a previous work, have been used.

Using the experimental determinations of the percentage basicity of glasses, pB, resulting from spectroscopic measurements and also the calculated values, the fractions BO_3 , BO_4 , AlO_4 and AlO_6 have been determined.

Using the experimental data of the measured properties, mathematical functions have been assessed for these, depending on the oxide composition. The values obtained approximate with high confidence the experimental data, thus validating the proposed approach.

Una din căile de abordare a sistemelor oxidice vitroase este reprezentată de triada compoziție – structură – proprietăți.

În lucrarea prezentată au fost analizate o serie de sticle din sistemul $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3$. Pentru această analiză s-au utilizat o serie de valori ale unor proprietăți determinate de autori și prezentate în lucrări anterioare.

Pe baza determinărilor spectroscopice a bazicității sticlelor, evaluată prin indicatorul structural, ponderea bazicității, pB, și a valorilor calculate s-au determinat fracțiile de BO_3 , BO_4 , AlO_4 și AlO_6 (pentru sticlele considerate).

Utilizând datele experimentale pentru proprietățile măsurate, s-au stabilit relații de calcul explicite pentru acestea, în raport cu compoziția oxidică. Valorile calculate cu aceste relații au coincis foarte bine cu cele experimentale, ceea ce validează raționamentul utilizat.

Keywords: $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3$ glass, basicity, BO_3 , BO_4 , AlO_4 and AlO_6 , density, refraction index, thermal expansion coefficient, vitreous transition temperature

1. Introduction

The glasses obtained from the ternary system M_2O (MO) - Al_2O_3 - B_2O_3 (M^+ - alkali ion and M^{++} - alkali earth ion) contain one network formative oxide (B_2O_3), a network modifier oxide (M_2O or MO) and another one with intermediary role (Al_2O_3). To the same category belong also the glasses obtained in the ternary systems $\text{M}_2\text{O} - \text{Al}_2\text{O}_3 - \text{SiO}_2$ [1,2], M_2O (MO) - $\text{Al}_2\text{O}_3 - \text{P}_2\text{O}_5$ [3÷5] and quaternary ones $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{B}_2\text{O}_3 - \text{SiO}_2$ [6].

In all the cases, the nature and the content of alkali oxide determine their modification of the level of elementary entities structure. Therefore, Raman spectroscopy and magic angle spinning nuclear magnetic resonance (MAS-NMR) studies put in evidence an $\text{AlO}_6 \leftrightarrow \text{AlO}_4$ conversion, sometimes with AlO_5 formation, for glasses based on SiO_2 and P_2O_5 [4].

Unlike these vitreous systems, aluminoborate glasses show a more complex structure. In this case, besides the existence of aluminum's double coordinated structural entities, a $\text{BO}_3 \leftrightarrow \text{BO}_4$ conversion also occurs. Unfortunately, experimental methods did not provide accurate

information regarding the weight of various types of structural entities for these glasses [7].

The present work, studies several glasses having a molar chemical composition $(35-x)\text{Na}_2\text{O}\cdot x\text{Al}_2\text{O}_3\cdot 65\text{B}_2\text{O}_3$, where $x = 0; 5; 10; 12.5; 15; 17.5$. Several properties have been experimentally determined for these glasses, among them – the basicity. This property has been evaluated using the percentage basicity pB, both calculated and experimentally measured. The percentages of different types of structural entities have been calculated using a fit method relying on the condition: $|\text{pB}^{\text{experimental}} - \text{pB}^{\text{calculated}}| \rightarrow \text{minimum}$.

The method has been previously used successfully by authors for aluminum coordination number establishing in glasses belonging to the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ system [8], when the predicted data has been verified by MAS-NMR results [4].

The method has also been used for establishing the lithium coordination number in glass belonging to the composition of lithium disilicate [9]. The calculated value was confirmed by neutron diffraction measurements [10].

All this structural transformations will determine the properties changes. In addition, the

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properties – structural entities correlation may explain the way in which properties vary with the variation of oxide composition.

2. Theoretical background

2.1. Alkali borate glasses

In relation with the glasses from ternary systems with network formative oxides SiO₂ or P₂O₅, the Na₂O-Al₂O₃-B₂O₃ ones are less studied, although they show interest from both structural point of view and also for their applications.

Figure 1 shows the phase diagram of the analyzed system [11].

As mentioned before, the focus of the study falls on several glasses having a molar chemical composition (35-x)Na₂O.xAl₂O₃.65B₂O₃.

Practically, 6 glasses have been elaborated, their composition being showed in Table 1. At the same time, the ternary vitreous oxide systems can be characterized from the composition point of view by means of modules **R** and **k**. Table 1 also shows the values of modules **R** and **k** deduced from the oxide composition of the 6 studied glasses.

For the studied oxide system, a function of **x** can be attributed to **R** and **k**:

$$R = (35 - x) / 65 = 0.5385 - 0.015 \cdot x$$

$$k = x / (35 - x) \quad (1)$$

For the 6 synthesized glasses, the Al₂O₃ content is expressed as fractions of AlO₄ and AlO₆, noted **a**, respectively **1-a** and the B₂O₃ content is expressed as fractions of BO₃ and BO₄ noted **b**, respectively **1-b**. At the same time, only one of the obtained glasses, G1 = 35N-65B, belongs to a binary system, Na₂O- B₂O₃, whose data are sufficient for an exact determination of the **b** value.

The introduction of alkali oxides in the structure of B₂O₃ determines the formation of BO₄ groups, together BO₃ groups. The BO₄ fraction (**1-b**) is determined by the effective oxide composition of the glass. For the alkali borate glasses, using the data provided, especially from the NMR and MAS-NMR measurements, it stands out that as the alkali oxide percentage is growing, a conversion from tri-coordinated boron (BO₃) to tetra-coordinated boron (BO₄) occurs. At **x** values below 33 molar % the tetra-coordinated boron

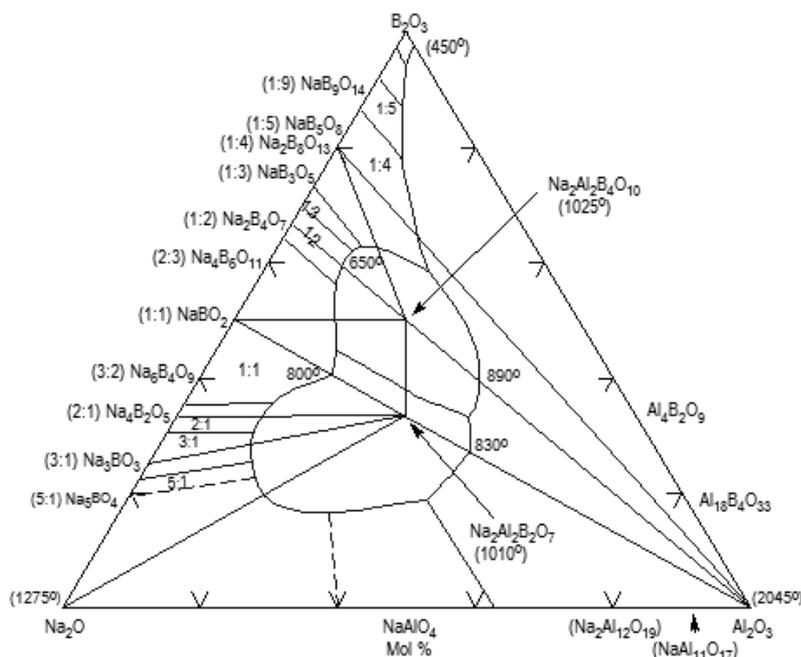


Fig. 1- Phase diagram of Na₂O-Al₂O₃-B₂O₃ system
Diagrama de fază a sistemului Na₂O - Al₂O₃ - B₂O₃ [11]

Table 1

Composition characterization of synthesized glasses / Caracterizarea compozițională a sticlelor sintetizate

Glass no. Nr. sticlă	Na ₂ O [mol. %]	x = Al ₂ O ₃ [mol. %]	B ₂ O ₃ [mol. %]	R = [mol. % M ₂ O] / [mol. % B ₂ O ₃]	k = [mol. % Al ₂ O ₃] / [mol. % M ₂ O]
G1	35	0	65	0.5385	0.00
G2	30	5	65	0.4615	0.1667
G3	25	10	65	0.3846	0.4000
G4	22.5	12.5	65	0.3462	0.5556
G5	20	15	65	0.3077	0.7500
G6	17.5	17.5	65	0.2692	1.0000

fraction is defined as $N_4 = R = [\text{mol. \% } M_2O] / [\text{mol. \% } B_2O_3]$. The minimum value for $(1-b) \equiv (BO_4)$ is 0.4 for $x = 33\%$, respectively, 0.5 for $x = 40\%$ [12,13], after which N_4 decreases again down to 0, for $R = 2$.

At the same time, Zhong and Bray [14] show that the BO_4 fraction in borate glasses is determined by both oxide composition and nature of alkali cation. Therefore, if $R = 0.33$, the BO_4 fraction is equal to $1-a = 0.45$ in glasses containing Li_2O and only 0.3 in those with Cs_2O .

Chryssikos et al. [15] confirm these results mentioning that in the Li, Na, K, Rb and Cs oxide series, the decrease of minimum value N_4 for BO_4 is proportional with the alkali ion radius. In context, Figure 2 shows the variation of N_4 fraction in relation to the basicity of the B_2O_3 alkali oxide partner for the composition of the diborate ($R = 0.33$) evaluated by pB.

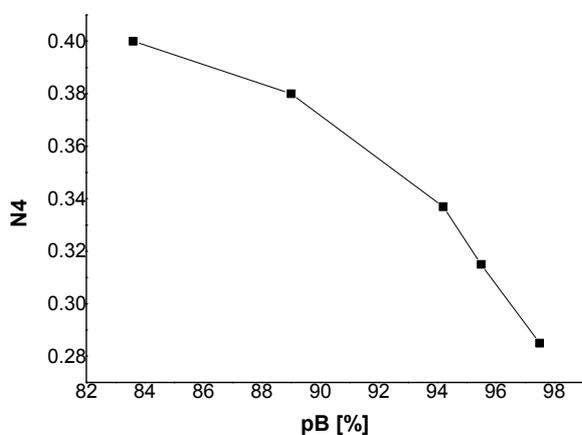


Fig. 2 - Variation of N_4 fraction as function of the percentage basicity for alkali diborate vitreous systems ($R = 0.33$) / Variația fracției de N_4 în funcție de ponderea bazicității pentru sistemele vitroase diboratice alcaline ($R = 0.33$).

The change of BO_3 / BO_4 ratio in alkali borate glasses due to alkali ion nature [16] is determining both the type of structural entity and also their share in characterized glasses that have the same R value.

For example, for $R = 0.33$, Table 2 shows the structural entity types that are present in 3 different alkali borate glasses [17] with the diborate composition and their basicity.

In the original work, the existence of different types of structural entities present in the 3 types of vitreous systems correlate with the alkali ion radius. Moreover, the influence of alkali oxide basicity it not to be neglected (Fig. 2).

Using Raman spectroscopy, the results of article [18] confirm the presence of a maximum value for N_4 at $x = 30\%$ in glasses from the system $Na_2O - B_2O_3$ and the exclusive existence of BO_3 and BO_4 as structural entities.

The research done by Baltă and Radu [19] confirms that for alkali borate glasses, the maximum fraction of BO_4 depends on the nature of alkali oxide, more specifically on the ratio between percentage basicity and the alkali cation radius.

Ducel et al., by studying a series of glasses from the system $Na_2O - B_2O_3 - P_2O_5$ [20], by ^{11}B NMR, determine that the BO_4 fraction is 0.47 for the glass composition of $x = 0.333$ and, respectively, $(1-a) \approx 0.5$ for a glass with $x = 0.35$ ($R = 0.538$).

The boron coordination change in relation with oxygen from 3 to 4 in alkali borate glasses induces changes for other structural features:

- increase in inter-nucleus bond length $B - O$, $d(B - O)$, from 0.136 nm up to 0.147 nm;
- decrease in bond energy, $E(B - O)$, from 514,8 kJ/mol down to 397,6 kJ/mol;
- increase of pB from 44.8% up to 54.4% (with direct implications on effective charge of atoms that form chemical bonds, polarizability of oxygen ion etc.).

The effects of these structural alterations are reflected on the properties of the glasses, in particular glass transition temperature, T_g , linear thermal expansion coefficient, α , refractive index, n , density, d , but not only [21÷23].

It is to be noted that, for example, in the case of molten glasses from $Na_2O - B_2O_3$ oxide system following different cooling paths, changes in the fraction $N_4 = 1-a$ were not registered. Thus, for a glass composition of 5N-95B, $N_4 = 11.6\%$, while for a glass having the molar formula 30N-70B, $N_4 = 45.8 \pm 5\%$, regardless of how the melt cooling process is done [24].

2.2. Ternary glasses in $Na_2O - Al_2O_3 - B_2O_3$ system. Structural elements

The introduction of Al_2O_3 in alkali borate glasses composition increases the thermodynamic stability of vitreous systems. This feature is evident even after small additions of Al_2O_3 .

From the structural point of view, the addition of Al_2O_3 to systems such as $M_2O (MO) - B_2O_3$ determines a competition between the cations of Al and B in terms of the number of oxygen ions contained in the first coordination

Table 2

Structural entity types and percentage basicity for alkali borate glasses
Tipuri de entități structurale și ponderea bazicității în sticle alcalino-boratice [17]

No.	Oxide Composition Compoziția oxidică	Cation radius Raza cationului [nm]	Structural entities Entități structurale	pB [%]
1	$Li_2O \cdot 2B_2O_3$	0.068	diborate	60.3
2	$Na_2O \cdot 2B_2O_3$	0.097	di-pentaborate triborate	61.2
3	$K_2O \cdot 2B_2O_3$	0.133	diborate di-triborate	61.9

sphere. As a consequence, structural entities of BO₃ and BO₄ or AlO₄, AlO₆ and sometimes AlO₅ may form.

Some of the first information on obtaining M₂O (MO) – Al₂O₃ – B₂O₃ systems type glasses dates back to 1970. However, more precise information on their structure were obtained after about two decades, with the development of more performant spectrometric methods for structural characterization.

Dupree et al. [25], using MAS–NMR technique, outline the changes on the first coordination sphere of ²⁷Al during devitrification of glasses from MgO – Al₂O₃ – B₂O₃ system, of great interest to the study of ceramic materials. In this glasses, the Al[OB]₄ and Al[OAl]₄ entities are found in preferentially rapport relation to other members of the Al[OB]_{4-x}[OAl]_x series of x = 0 ÷ 4, according with ²⁷Al spectroscopy. Al[OB]₆ structural entities were not observed in crystallized glasses, unlike Al₁₈B₄O₃₃ composition crystals.

In aluminoborate glasses, ²⁷Al MAS–NMR showed that a significant fraction of Al is contained in AlO₅ and AlO₆. The presence of additional species complicates the structure, probably increasing the structural disorder and surely introducing new types of oxygen bridges which connect only BO₃, BO₄ or AlO₄ but changes the coordination balance with AlO₅ and AlO₆ groups. Recent ²⁷Al MAS–NMR analysis on similar compositions suggests that highly coordinated Al is only 3 ÷ 8% of total Al amount.

The spectra obtained using Multiple–Quantum Magic–Angle Spinning ¹⁷O NMR method [26] showed the parameters for different atoms that form bonds with oxygen: B – O – B, Al – O – B, Al[B] – O – Na. Borate glass with 33.3% mol. Na₂O presents diborate crystalline structure, when 37.5 % of B atoms are tetra-coordinated. Oxygen can couple 2 BO₄, 2 BO₃ or BO₄ and BO₃.

Analyzing some literature data of ¹¹B NMR regarding glasses from Na₂O – Al₂O₃ – B₂O₃ and CaO – Al₂O₃ – B₂O₃ systems, and personal obtained results on glasses from Na₂O – Al₂O₃ – B₂O₃ – SiO₂, El-Damrawi et al. [6] showed that oxygen ions introduced by the modifier oxide are first consumed in order to ensure coordination 4 of aluminum, respectively AlO₄. The remaining oxygen ions are used to ensure coordination 4 for boron, respectively the BO₃ ↔ BO₄ conversion. In the quaternary system, after achieving the maximum of BO₄ units, for k = 0.14, a decrease takes place for molar ratios Al₂O₃] / [Na₂O] ≥ 1, when the BO₄ entities disappear.

³¹P MAS and ¹¹B NMR methods were used to determine the fractions of tri and tetra-coordinated B in the borosilicate systems [27,28], Na₂O – B₂O₃ – SiO₂ and borophosphate [20] with (1-x)NaPO₅.xNa₂B₄O₇ chemical composition.

In the case of alkali borosilicate glasses, it is considered that an introduced alkali oxide is incorporated into the borate structure up to a certain limit value, **R₀**. Above this value (which also depends on the module **k**) the oxide is used also by the silicate network. It is therefore accepted that the compositional parameter **R** has two components, **R_{Si}** and **R_B**, **R_{Si} + R_B = R** [27]. This approach can be extended to glasses from M₂O – Al₂O₃ – B₂O₃ system, where the alkali oxide is primarily used for converting AlO₆ ↔ AlO₄, up to a limit value **R₀**. The rest of the alkali oxide is incorporated into the borate network too. In this case, the **R_{Al} + R_B = R** condition is provided.

¹¹B NMR studies on glasses with (1-x)NaPO₅.xNa₂B₄O₇ composition [20] showed that in the region abounding in boron, BO₄ fraction tends to the value 0.47, corresponding to vitreous diborate too.

From the information briefly presented, we can state that:

- for the alkali borate glass, G₁, the types of structural entities may be defined both in terms of quality and quantity (with a fairly high degree of certainty);
- for the ternary glasses, G₂ ÷ G₆, the nature of structural entities is known; will be determined their quantitative distribution (depending on the oxide composition);
- finally, it is of great interest to highlight how the properties of studied glasses depend on the distribution of structural entities.

3. Results and discussions

3.1. Experimental procedure

The following compositions were made: (35-x).Na₂O.xAl₂O₃.65B₂O₃, (x = 0; 5; 10; 12.5; 15; 17.5% mol.). The raw materials: NaCO₃, H₃BO₃ and Al₂O₃ were melted in platinum crucibles around 1000°C and maintained at this temperature for 3 hours to reach the structural chemical equilibrium. All the obtained samples were treated at T_g, according to literature data, the temperature being then determined by dilatometry and corrected for the next series of samples. The samples were cooled quickly by pressing in graphite molds [21,22].

The linear thermal expansion coefficient, α, and vitreous transition temperature, T_g, were determined for the obtained samples by dilatometry (with vertical differential dilatometer with quartz glass tube at the heating rate of 3°C/min.). The density, d, (with hydrostatic balance) and the refractive index, n, (with Abbe refractometer) were also determined [21,22]

For the experimental determination of

basicity, pB_e , we used the method presented by Baltă [29]. In this respect, every considered composition was synthesized, doped with 0,1 % at. Cu^{2+} (introduced as CuO). The experimental value used as basicity measure is the minimum energy expressed as wavenumber, to which the absorption occurs by $Cu^{2+}O_6$ complex charge transfer. Thus, glass samples doped with Cu^{2+} and not doped samples as witness were prepared for every considered composition.

Based on the wavenumber ν corresponding to UV maximum absorption peak, by a UV-VIS spectrophotometer M40, pB_e was determined using the following relation [29]:

$$pB_e = 151 - 0.00259 \cdot \nu \quad (2)$$

3.2. Setting fractions $a \equiv AlO_4$ and $b \equiv BO_3$

For oxide vitreous systems, a series of explicit relationships between the properties P and oxide composition x_i , $i = \overline{1, n}$, were put in evidence. They have the form:

$$P = f(x_1, x_2, \dots, x_i, \dots, x_n) \quad (3)$$

where the correlation function f can be linear or

non-linear, and $\sum_{i=1}^n x_i = 1$

If a linear correlation between variables is accepted, one can write:

$$P_j = \sum_{i=1}^n f_{ij} \cdot x_i \quad j = \overline{1, m} \quad (4)$$

where P_j is the j property; m - the number of properties of the vitreous system; f_{ij} - characteristic factors of the property j and the oxide i . Normalization condition must be fulfilled,

$$\sum_{i=1}^n x_i = 1.$$

For the analyzed ternary system, a property P_j can be described by an additive relationship such as:

$$P_j = f_{1j} \cdot x_1 + f_{2j} \cdot ax_2 + f_{3j} \cdot (1-a)x_2 + f_{4j} \cdot bx_3 + f_{5j} \cdot (1-b)x_3 \quad (5)$$

where $\sum_{i=1}^3 x_i = 1$; $a \equiv AlO_4$; $(1-a) \equiv AlO_6$;

$$b \equiv BO_3; (1-b) \equiv BO_4$$

Relationship (5) can be used in two ways:

- when the variables P_j , x_i , a and b are known, the values for f_{ij} , $i = \overline{1, n}$ factors can be established based on $n-1$ measurements;

- if the parameters P_j , x_i , $i = \overline{1, n}$ and the factors f_{ij} are known, the structural coefficients a and b can be calculated; in order to do this, besides the experimental value of the property P_j^{exp} , it is necessary

to determine the calculated one, P_j^{calc} .

In this case, the parameters a and b are calculated from the condition:

$$\min |P_j^{exp} - P_j^{calc}| \quad (\text{ideally } P_j^{exp} = P_j^{calc}) \quad (6)$$

To use this method it is necessary to find an experimental property who is sensitive to changes in the coefficients a and b . In addition, the factors f_{ij} should be known.

The percentage basicity was considered the reference property for calculating the structural parameters $a \equiv AlO_4$ and $b \equiv BO_3$. The motivation is based on the fact that in vitreous oxide systems, the percentage basicity is a structural parameter that closely correlates with a series of classical stereo-energetic characteristics [30,31]. In the same time, strong correlations between the properties of glasses and pB were put in evidence [30,31].

The algebraic expression for pB of the obtained glasses in the studied ternary system can be written as:

$$pB^{calc} = \frac{(35-x) \cdot M_{Na_2O} \cdot pB_{Na_2O} + (1-x) \cdot M_{Al_2O_3} \cdot a \cdot pB_{Al_2O_3} + x \cdot M_{Al_2O_3} \cdot a \cdot pB_{Al_2O_3} + 65 \cdot M_{B_2O_3} \cdot b \cdot pB_{B_2O_3} + 65 \cdot M_{B_2O_3} \cdot (1-b) \cdot pB_{B_2O_3}}{(35-x) \cdot M_{Na_2O} + x \cdot M_{Al_2O_3} + 65 \cdot M_{B_2O_3}} \quad (7)$$

where: M_{XO} and pB_{XO} represent the molecular weight, respectively the percentage basicity for XO oxide [30].

In order to determine the values of the structural coefficients a and b , besides relationship (7), it is necessary to fulfill the conditions:

$$(pB^{exp} - pB^{calc})^2 = \text{minim} \quad (8)$$

$$0 < a \leq 1; \quad 0.53 \leq b \leq 1 \quad (9)$$

Solving the system of restrictions (8) and (9) for $x = \text{const.}$, has lead to the values presented in Table 3. The relative deviation ϵ_r values are also presented, and calculated with the formula:

$$\epsilon_r = (pB^{exp} - pB^{calc}) \times 100 / pB_{exp} \quad [\%] \quad (10)$$

From the data centralized in Table 3, the following conclusions can be made:

Table 3

The values for structural coefficients **a** and **b** depending on the glass composition
 Valorile coeficienților structurali **a** și **b** în funcție de compoziția sticlei

x [mol. %]	Na ₂ O [wt. %]	Al ₂ O ₃ [wt. %]	B ₂ O ₃ [wt. %]	a	1-a	b	1-b	pB ^{calc} [%]	pB ^{exp} [%]	ε _r [%]
0	32.29	0.00	67.71	0	0	0.53 *	0.47 *	62.14	--- **	---
5	26.88	7.37	65.75	---	---	---	---	---	61.89	---
10	21.77	14.33	63.90	0.655	0.345	0.516	0.484	60.35	60.35	0.00
12.5	19.32	17.66	63.02	0.927	0.073	0.786	0.214	57.76	57.76	0.01
15	16.94	20.90	62.16	1	0	1	0	55.83	55.17	1.19
17.5	14.62	24.06	61.32	0.934	0.066	0.793	0.207	56.72	56.72	0.00

* literature values

** for percentage basicity, pB, were not made experimental determination

- in almost all chemical compositions of examined vitreous system coexist for both B and Al, structural entities with defined coordination; the only exception is the glass containing 20% mol. Na₂O, when only AlO₄ and BO₃ can be found;
- an increase in the percentage of alkali oxide in the analyzed vitreous system Na₂O – Al₂O₃ – B₂O₃ involves a decrease in BO₄ fraction, similar to what happens in alkali borate systems;
- an increase in the Na₂O content up to 20 % implies an increase in the percentage of AlO₄ to the prejudice of AlO₆ structural entities; the behavior is reversed, as attested by a series of data of literature, from the system Na₂O - Al₂O₃ - SiO₂ [7]. In this system, the appearance of AlO₄ units occurs after the oxide composition satisfies the condition Na₂O / Al₂O₃ > 1.

3.3. Properties - structural entities correlations

Usually, the literature put in evidence a series of relations for glass properties calculation in function of oxide composition, as the equation (4).

Taking in account that the properties of vitreous systems are determined by oxide composition and other processing parameters such as melting history, thermo-mechanical history, etc., all the variables associated with the synthesis, followed by the formation of the vitreous system

itself are responsible for the stereo-chemical characteristics of the system, respectively for the properties of glass. For this reason, equation (4) is

$$\text{rewritten under the form: } P_j = \sum_{i=1}^n S_{ij} \cdot x_i \quad (11)$$

in which S_{ij} is the structural entity's value of property P_j (n – number of structural entities for the considered structural level).

For each P_j property, in order to calculate

the structural parameters S_{ij} associated with the ternary glass systems, equation (11) is rewritten in relation to glasses G1, G3 ÷ G6. The result is a 5 x 5 linear system which easily offers solutions

for S_{ij} :

$$P_{ik} = \sum_{i=1}^n S_{ijk} \cdot x_{ik} \quad j = \overline{1,4}$$

$$k = \{1,3,4,5,6\} \quad (12)$$

In the system (12), the P_{ik} values represent the experimentally determined density, refraction index, linear thermal expansion

Table 4

Values of structural factors S_{ij} for entities belonging to studied glasses

Valorile factorilor structurali S_{ij} pentru entitățile tipice sticlelor studiate.

Property / Proprietate	Structural entity type / Tip entitate structurală				
	Na ₂ O	AlO ₄	AlO ₆	BO ₃	BO ₄
Density / Densitate, d [g/cm ³]	7.276	4.184	4.059	0.13	0.01
Refraction index / Indice de refracție, n	4.676	3.301	3.284	0.015	0.0016
Thermal expansion coefficient Coeficient de dilatare termică, α [K ⁻¹ .10 ⁷]	450.7	342.1	25.6	- 105.8	- 16.1
Vitreous transition temperature Temperatura tranziției vitroase, T _g , [°C]	1676.3	1130.3	1089	- 116.1	- 62.2

Table 5

Comparison between calculated values (calc) from equations (13) ÷ (16) and the measured experimental (exp) ones for d, n, α and T_g
 Comparație între valorile calculate (calc) cu relațiile (13) ÷ (16) și cele măsurate experimental (exp), pentru d, n, α și T_g

Glass/ Sticlă	x [mol%]	Property / Proprietate											
		Density / Densitate, d [g/cm ³]			Refraction index / Indice de refracție, n			Thermal expansion coefficient / Coeficient de dilatate termică, α [10 ⁷ ·K ⁻¹]			Vitreous transition temperature / Temperatura tranziției vitroase T _g [°C]		
		d ^{calc}	d ^{exp}	ε _r [%]	n ^{calc}	n ^{exp}	ε _r [%]	α ^{calc}	α ^{exp}	ε _r [%]	T _g ^{calc}	T _g ^{exp}	ε _r [%]
G1	0	2.399	2.4	0.03	1.5157	1.5162	0.03	102.5	102.5	0.05	480	480	0.04
G2	5	----	2.338	----	----	1.5085	----	----	95.1	----	----	472	----
G3	10	2.223	2.227	0.16	1.4955	1.4965	0.06	91.6	88.6	3.43	467	464	0.72
G4	12.5	2.209	2.218	0.42	1.4937	1.4951	0.09	88.8	80.8	9.95	457	448	2.02
G5	15	2.188	2.188	0.01	1.4912	1.4923	0.07	82.1	82.1	0.02	448	448	0.01
G6	17.5	2.133	2.133	0.00	1.4850	1.4862	0.08	89.7	89.7	0.01	452	452	0.00

$$d = 7.276 \cdot f_{\text{Na}_2\text{O}} + 4.184 \cdot a \cdot f_{\text{Al}_2\text{O}_3} + 4.059 \cdot (1-a) \cdot f_{\text{Al}_2\text{O}_3} + 0.13 \cdot b \cdot f_{\text{B}_2\text{O}_3} + 0.01 \cdot (1-b) \cdot f_{\text{B}_2\text{O}_3} \quad (13)$$

$$n = 4.676 \cdot f_{\text{Na}_2\text{O}} + 3.301 \cdot a \cdot f_{\text{Al}_2\text{O}_3} + 3.284 \cdot (1-a) \cdot f_{\text{Al}_2\text{O}_3} + 0.0148 \cdot b \cdot f_{\text{B}_2\text{O}_3} + 0.0016 \cdot (1-b) \cdot f_{\text{B}_2\text{O}_3} \quad (14)$$

$$\alpha = 450.7 \cdot f_{\text{Na}_2\text{O}} + 342.1 \cdot a \cdot f_{\text{Al}_2\text{O}_3} + 25.6 \cdot (1-a) \cdot f_{\text{Al}_2\text{O}_3} - 105.8 \cdot b \cdot f_{\text{B}_2\text{O}_3} - 16.1 \cdot (1-b) \cdot f_{\text{B}_2\text{O}_3} \quad (15)$$

$$T_g = 1676.3 \cdot f_{\text{Na}_2\text{O}} + 1130.3 \cdot a \cdot f_{\text{Al}_2\text{O}_3} + 1089 \cdot (1-a) \cdot f_{\text{Al}_2\text{O}_3} - 116.1 \cdot b \cdot f_{\text{B}_2\text{O}_3} - 62.2 \cdot (1-b) \cdot f_{\text{B}_2\text{O}_3} \quad (16)$$

coefficient and T_g, for the 5 considered oxide compositions.

By solving the system (12) the values of the structural factors S_{ij} have been determined for the structural entity i and property j . The values are presented in Table 4.

Data from Table 4 permit the explicit calculation of the properties, as a function of gravimetric fractions and types of structural entities. For glasses belonging to the studied ternary system it results the above equations (13) – (16), oxides are expressed as gravimetric fractions.

The equations offer the possibility to calculate the properties of interest d^{calc} , n^{calc} , α^{calc} , T_g^{calc} in relation to the type and distribution of structural entities. These values can be compared with data sets representing experimental values determined by authors: d^{exp} , n^{exp} , α^{exp} and T_g^{exp}

(Table 5). For each property it is also shown the relative deviation ε_r .

The comparative analysis of these values leads to the conclusion that the two sets of values are very closed, fact that certifies the validity of the presented considerations.

4. Conclusions

For studying glasses belonging to the Na₂O – Al₂O₃ – B₂O₃ system, in relation to the effective oxide composition, the question is to establish the quantity of BO₃/BO₄ and AlO₄/AlO₆ structural entities.

The establishing of molar fractions of structural entities has been done on the basis of experimental values determined using the basicity of obtained glasses. The fit method was applied for the basicity results (evaluated with the percentage basicity, pB) using the values obtained by measurements.

Once established the percentages of different types of structural entities with respect to the oxide composition of glass, a set of functions has been set to express several properties in relation to their oxide composition. The property values (for density, refraction index, linear thermal expansion coefficient, vitreous transition temperature) calculated with the determined relations has statistically fitted the experimental ones, thus proving the correctness of proposed method.

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