1. Introduction

The glasses obtained from the ternary system M₂O (MO) - Al₂O₃ - B₂O₃ (M⁺ - alkali ion and M** - alkali earth ion) contain one network forming oxide (B₂O₃), a network modifier oxide (M₂O or MO) and another one with intermediary role (Al₂O₃). To the same category belong also the glasses obtained in the ternary systems M₂O - Al₂O₃ - SiO₂ [1,2], M₂O (MO) - Al₂O₃ - P₂O₅ [3-5] and quaternary ones Na₂O - Al₂O₃ - B₂O₃ - SiO₂ [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 AlO₆ ↔ AlO₄ conversion, sometimes with AlO₅ formation, for glasses based on SiO₂ and P₂O₅ [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 BO₃ ↔ BO₄ 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)Na₂O·xAl₂O₃·65B₂O₃, 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: [pB<sub>experimental</sub> - pB<sub>calculated</sub>] → minimum.

The method has been previously used successfully by authors for aluminum coordination number establishing in glasses belonging to the Na₂O·Al₂O₃·P₂O₅ 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...
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 deducted 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:

\[
R = \frac{(35 - x)}{65} = 0.5385 - 0.015x
\]

\[
k = \frac{x}{(35 - x)}
\]  

(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

<table>
<thead>
<tr>
<th>Glass no.</th>
<th>Na₂O [mol. %]</th>
<th>x = Al₂O₃ [mol. %]</th>
<th>B₂O₃ [mol. %]</th>
<th>R = [mol. % M₂O] / [mol. % B₂O₃]</th>
<th>k = [mol. %Al₂O₃] / [mol. % M₂O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>35</td>
<td>0</td>
<td>65</td>
<td>0.5385</td>
<td>0.00</td>
</tr>
<tr>
<td>G2</td>
<td>30</td>
<td>5</td>
<td>65</td>
<td>0.4615</td>
<td>0.1667</td>
</tr>
<tr>
<td>G3</td>
<td>25</td>
<td>10</td>
<td>65</td>
<td>0.3846</td>
<td>0.4000</td>
</tr>
<tr>
<td>G4</td>
<td>22.5</td>
<td>12.5</td>
<td>65</td>
<td>0.3462</td>
<td>0.5556</td>
</tr>
<tr>
<td>G5</td>
<td>20</td>
<td>15</td>
<td>65</td>
<td>0.3077</td>
<td>0.7500</td>
</tr>
<tr>
<td>G6</td>
<td>17.5</td>
<td>17.5</td>
<td>65</td>
<td>0.2692</td>
<td>1.0000</td>
</tr>
</tbody>
</table>
fraction is defined as $N_4 = R = [\text{mol. } \% \text{ } \text{M}_2\text{O}] / [\text{mol. } \% \text{ } \text{B}_2\text{O}_3]$. The minimum value for $1 - b = (\text{BO}_4)$ is 0.4 for $x = 33\%$, respectively, 0.5 for $x = 40\%$, 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$_2$O and only 0.3 in those with Cs$_2$O.

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$_2$O$_3$ alkali oxide partner for the composition of the diborate ($R = 0.33$) evaluated by $p_B$.

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$_2$O – B$_2$O$_3$ 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.

The boron coordination change in relation with oxygen from 3 to 4 in alkali borate glasses inducts changes for other structural features:
- increase in inter-nucleus bond length B – O, $d(\text{B} – \text{O})$, from 0.136 nm up to 0.147 nm;
- decrease in bond energy, $E(\text{B} – \text{O})$, from 514.8 kJ/mol down to 397.6 kJ/mol;
- increase of $p_B$ 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, $\alpha$, 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$_2$O – B$_2$O$_3$ 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$_2$O – Al$_2$O$_3$ – B$_2$O$_3$ system. Structural elements

The introduction of Al$_2$O$_3$ in alkali borate glasses composition increases the thermodynamic stability of vitreous systems. This feature is evident even after small additions of Al$_2$O$_3$.

From the structural point of view, the addition of Al$_2$O$_3$ to systems such as M$_2$O (MO) – B$_2$O$_3$ determines a competition between the cations of Al and B in terms of the number of oxygen ions contained in the first coordination sphere. 

#### Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Oxide Composition</th>
<th>Cation radius [nm]</th>
<th>Structural entities</th>
<th>$p_B$ [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Li$_2$O 2B$_2$O$_3$</td>
<td>0.068</td>
<td>diborate</td>
<td>60.3</td>
</tr>
<tr>
<td>2</td>
<td>Na$_2$O 2B$_2$O$_3$</td>
<td>0.097</td>
<td>di-pentaborate</td>
<td>61.2</td>
</tr>
<tr>
<td>3</td>
<td>K$_2$O 2B$_2$O$_3$</td>
<td>0.133</td>
<td>diborate</td>
<td>61.9</td>
</tr>
</tbody>
</table>
sphere. As a consequence, structural entities of BO₃ and BO₄ or AlO₄, AlO₅ and sometimes AlO₆ 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[OAl]₄ 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 AlO₄ 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 AlO₃ 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 following compositions were made:
(35–x)Na₂O.xAl₂O₃.65B₂O₃, (x = 0; 5; 10; 12.5; 15; 17.5% mol.). The raw materials: Na₂CO₃, H₃BO₃ and Al₂O₃ were melted in platinum crucibles at Tₕ = 1800°C and maintained at this temperature for 3 hours to reach the structural chemical equilibrium. All the obtained samples were treated at Tₕ, 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, Tᵥ, 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

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, R₆. 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, R₆ and R₈. R₆ + R₈ = 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 R₆. The rest of the alkali oxide is incorporated into the borate network too. In this case, the R₆ + R₈ = R condition is provided.

11B NMR studies on glasses with (1– x)NaPO₄.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: Na₂CO₃, 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 Tᵥ, 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, Tᵥ, 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
basicty, \( pB_c \), we used the method presented by Baltă [29]. In this respect, every considered composition was synthesized, doped with 0.1 % at. \( \text{Cu}^{2+} \) (introduced as \( \text{CuO} \)). The experimental value used as basicty measure is the minimum energy expressed as wavenumber, to which the absorption occurs by \( \text{Cu}^{2+}\text{O}_6 \) complex charge transfer. Thus, glass samples doped with \( \text{Cu}^{2+} \) and not doped samples as witness were prepared for every considered composition.

Based on the wavenumber \( \nu \) corresponding to UV maximum absorption peak, by a UV-VIS spectrophotometer M40, \( pB_c \) was determined using the following relation [29]:

\[
pB_c = 151 - 0.00259 \cdot \nu
\]  

(2)

### 3.2. Setting fractions \( a = \text{AlO}_4 \) and \( b = \text{BO}_3 \)

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

\[
P = f (x_1, x_2, \ldots, x_i, \ldots, x_n)
\]

(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:

\[
P_j = \sum_{i=1}^{n} f_{ij} \cdot x_i \quad j = 1, m
\]

(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:

\[
P_j = f_{ij} \cdot x_i + f_{j2} \cdot ax_2 + f_{j3} \cdot (1-a)x_2 + f_{j4} \cdot bx_3 + f_{j5} \cdot (1-b)x_3
\]

(5)

where \( \sum_{i=1}^{3} x_i = 1 \); \( a = \text{AlO}_4; \ (1-a) = \text{AlO}_6; \)

\( b = \text{BO}_3; \ (1-b) = \text{BO}_4 \).

Relationship (5) can be used in two ways:

- if the parameters \( f_{ij}, x_i, \ i = 1, n \) 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 \( P_j^{\text{exp}} \), it is necessary to determine the calculated one, \( P_j^{\text{calc}} \).

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

\[
\min \left| P_j^{\text{exp}} - P_j^{\text{calc}} \right| \quad \text{(ideally } P_j^{\text{exp}} = P_j^{\text{calc}} \text{)}
\]

(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 \( a = \text{AlO}_4 \) and \( b = \text{BO}_3 \). 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:

\[
pB^{\text{calc}} = \frac{(35-x)\cdot M_{\text{Al2O3}} \cdot pB_{\text{Al2O3}} + (1-x) \cdot M_{\text{BO3}} \cdot a \cdot pB_{\text{BO3}}}{(35-x)\cdot M_{\text{Al2O3}} + x \cdot M_{\text{BO3}}} + \frac{x \cdot M_{\text{Al2O3}} \cdot b \cdot pB_{\text{BO3}} + 65 \cdot M_{\text{BO3}}}{65 + (1-x) \cdot M_{\text{Al2O3}} + 65 \cdot M_{\text{BO3}}}
\]

(7)

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

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

\[
(pB^{\text{exp}} - pB^{\text{calc}},)^2 = \text{minim}
\]

\[
0 < a \leq 1; \ 0.53 \leq b \leq 1
\]

(8)

(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 \( \varepsilon \), values are also presented, and calculated with the formula:

\[
\varepsilon = \frac{(pB^{\text{exp}} - pB^{\text{calc}}) \times 100}{pB^{\text{exp}}} \%
\]

(10)

From the data centralized in Table 3, the following conclusions can be made:
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 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 $S_{ij}$:

$$ P_{ik} = \sum_{j=1}^{n} S_{ijk} \cdot x_{ik} \quad j = 1,4 \quad k = \{1,3,4,5,6\} \quad (12) $$

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

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

<table>
<thead>
<tr>
<th>Property / Proprietate</th>
<th>Structural entity type / Tip entitate structurală</th>
</tr>
</thead>
<tbody>
<tr>
<td>Densitate / d [g/cm$^3$]</td>
<td>Na$_2$O</td>
</tr>
<tr>
<td>7.276</td>
<td>4.184</td>
</tr>
<tr>
<td>Índice de refracción, n</td>
<td>Refraction index</td>
</tr>
<tr>
<td>Coeficient de dilatare termică, $\alpha$ [K$^{-1}$10$^{-7}$]</td>
<td>Thermal expansion coefficient</td>
</tr>
<tr>
<td>Temperatura tranziției vitroase, $T_g$ [°C]</td>
<td>Vitreous transition temperature</td>
</tr>
</tbody>
</table>
căderea, fără a confunda reactivitatea cu spusa. Reactivitatea este definită ca cantitatea de reactant disponibilă, care este activă pentru a realiza reacția, în timp ce spusa este cantitatea de reactant care nu este utilizată în reacție. În cazul reacționărilor, reactivitatea este adesea mai mare decât spusa, deoarece reactivitatea este definită ca cantitatea de reactant care este disponibilă pentru a realiza reacția, în timp ce spusa este cantitatea de reactant care nu este utilizată în reacție.


d=7.276 \cdot f_{Na_2O} + 4.184 \cdot f_{Al_2O_3} + 4.059 \cdot (1-a) \cdot f_{Al_2O_3} + 0.13 \cdot b \cdot f_{B_2O_3} + 0.01 \cdot (1-b) \cdot f_{B_2O_3} \quad (13)

n=4.676 \cdot f_{Na_2O} + 3.301 \cdot f_{Al_2O_3} + 3.284 \cdot (1-a) \cdot f_{Al_2O_3} + 0.0148 \cdot b \cdot f_{B_2O_3} + 0.0016 \cdot (1-b) \cdot f_{B_2O_3} \quad (14)

\alpha=450.7 \cdot f_{Na_2O} + 342.1 \cdot f_{Al_2O_3} + 25.6 \cdot (1-a) \cdot f_{Al_2O_3} - 105.8 \cdot b \cdot f_{B_2O_3} - 16.1 \cdot (1-b) \cdot f_{B_2O_3} \quad (15)

T_g=1676.3 \cdot f_{Na_2O} + 1130.3 \cdot f_{Al_2O_3} + 1089 \cdot (1-a) \cdot f_{Al_2O_3} - 116.1 \cdot b \cdot f_{B_2O_3} - 62.2 \cdot (1-b) \cdot f_{B_2O_3} \quad (16)

The establishment 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.

**REFERENCES**


