PROPRIETĂȚILE OPTICE VERSUS COMPACTITATEA STRUCTURALĂ PENTRU STICLE DIN SISTEMUL Na₂O-Al₂O₃-B₂O₃
OPTICAL PROPERTIES VERSUS STRUCTURAL PACKING DENSITY FOR Na₂O-Al₂O₃-B₂O₃ GLASSES

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Six glasses belonging to the Na₂O-Al₂O₃-B₂O₃ oxide system with the molar composition $(35-x)Na_2O\cdot xAl_2O_3\cdot 65B_2O_3$ were synthesized. Refractive index, n, and density, d, were measured on these glasses; the experimental values were used to compute a series of optical properties: transmission, T, molar refractivity, R_m, mass refractivity, R_M, and specific refractivity, r.

Correlations between optical properties and chemical composition, glass features at the first structural level (molar volume, V_m) and compactness, C, were drawn.

It was concluded that glass compactness (a feature describing the atomic level – sub-nanoscale) is an influential parameter on optical properties of the glasses, which manifest on a macroscopic scale.

Un număr de șase sticle din sistemul oxidic Na₂O-Al₂O₃-B₂O₃ având compoziția molară $(35-x)Na_2O\cdot xAl_2O_3\cdot 65B_2O_3$ au fost sintetizate. Pe aceste sticle au fost măsurate indicele de refracție, n, densitatea, d. Valorile obținute au fost utilizate pentru calculul proprietăților optice ale sticlelor: transmisia, T, refracția molară, R_m, refracția masică, R_M, refracția specifică, r.

Au fost obținute corelații între proprietățile optice și compoziția chimică, caracteristici structurale la primul nivel structural (volumul molar, V_m) și compactitatea, C.

S-a evidențiat faptul că o caracteristică structurală la nivel atomic – compactitatea structurală – este un parametru care influențează proprietățile optice ale sticlelor, care se manifestă la scară macroscopică.

Keywords: glass, optical properties, structural compactness, correlations

1. Introduction

In oxide systems such as M₂O(M'O)-Al₂O₃-B₂O₃, M=Li, Na, K, M'=Mg, there were synthesized stable glasses for over 30 years. [1-3] These glasses are both scientifically and practically interesting because, depending on their chemical composition, reversible structural changes were recorded, such as: $[BO_3] \leftrightarrow [BO_4]$ and $[AlO_4] \leftrightarrow [AlO_6]$.

Recently, a series of glasses of the molar composition $(35-x)Na_2O\cdot xAl_2O_3\cdot 65B_2O_3$ have been obtained [4] and subjected to properties evaluation: density, refractive index, thermal expansion coefficient, glass-transition temperature and basicity percentage. These properties have been correlated with the oxide composition [3] and with a series of structural entities [4-6].

In this paper, it is studied the correlation between optical properties vs. oxide composition for these glasses, x=0..17.5% mol. Also, properties were evaluated against the structural compactness of the glasses at the atomic level (sub-nanometric scale).

2. Experimental data

Raw mixes were computed based on the oxide composition of the 6 glasses – codes G0-G5 –

Table 1.

Physical properties of the glasses
Proprietăți fizice ale sticlelor [4]

Glass code	x %mol Al₂O₃	d 10^3 kg·m⁻³	n
G0	0.0	2.400	1.5162
G1	5.0	2.338	1.5085
G2	10.0	2.227	1.4965
G3	12.5	2.218	1.4961
G4	15.0	2.188	1.4923
G5	17.5	2.133	1.4862
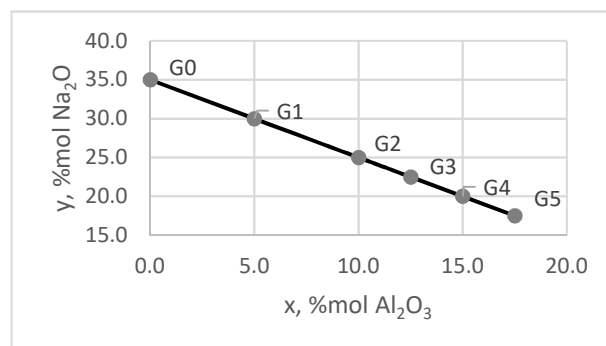
Fig. 1 - Oxide composition of the glasses / *Compoziția oxidică a sticlelor* (z = 65% mol. B₂O₃, $x+y+x$=100%)..

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provided in Figure 1. The raw mixes were processed according to description given in [4] and the resulting glasses were subjected to experimental determination of some physical properties, such as density *d* and refractive index *n* [4]. Collected data are given in Table 1; they were used to compute the optical properties: reflection, *R*, molar refractivity, *R_m*, mass refractivity, *R_M*, and specific refractivity, *r*.

3. Theoretical basis

3.1. Glass structural features

Viewed systemically, glass can be defined as a system made of number of structural entities, sufficiently strong and stable to provide the following features [7, 8]:
- short and, possibly, medium range order:
- lack of order at long distance (over 1-1.5nm);
- glass transition temperature, T_g.

Glass systems have a hierarchical structure in which nature of the entities differ, according to structural levels.

For the first level, the nature and the ratio between atoms (ions) – the simplest structural entities – can be considered. At the atomic structural level, a general chemical formula of the vitreous system can be written as: $aF \cdot bO \cdot c_1M_1 \cdot c_2M_2...$, with aF being the number of atoms (ions) that are network formers; bO - number of atoms (ions) of oxygen; c_iM_i - number of i atoms (ions) that are modifiers. Usual network formers have the F^{a+} (a being the oxidation number of the former as related to oxygen) ions diameters to be found in the range 0.07-0.18nm. If diameters corresponding to covalent bonds for F are considered, these can reach values between 0.16 and 0.28nm. The diameter of the O^{2-} ion is 0.14 nm while the covalent oxygen is of 0.60 nm. Modifiers are cations of diameters smaller than 0.5 nm.

The second structural level is being characterized by the existence of structural entities in the shape of elementary coordination polyhedra that are built according to the atoms' coordination numbers.

The elementary structural units have the formula $[XO_N]$, with $X=F/M_1/M_2/...$, N is X's coordination number as related to oxygen. Usually, N is 3 or/and 4 when $X=F$ or $N \geq 4$ for M_1, M_2, ...; in such cases, diameters of the spheres circumscribing coordination polyhedra $[XO_N]$ are less than 1 nm.

Consequently, the description of the glass structure for the first two structural levels can be made at a sub-nanometric scale (<1 nm).

At the third level, the structure is defined by a series of complex aggregates, having various chemical structures and size. These aggregates appear by interconnecting – through vertices – the elementary structural units. Types and weight of each structural aggregate depends on the extent on

which chemical structural equilibrium has been attained. At its turn, this one depends on chemical composition, temperature and melting time. At this level, the scale is nanometric.

The last structural level for oxide vitreous systems is characterized by the existence of microphase separation phenomenon. Their size can be found within nanometric-micrometric range.

3.2. Glass properties computation

The main issue concerning glass chemistry is to properly design a vitreous system to achieve predictable properties. For now, purely theoretical or experimental approaches have failed to provide a viable solution to the issue.

A first attempt to provide a solution is by using mathematical programming models; functions property-oxide composition drawn by a statistical analysis of experimental data by the means of design of experiments method [8]. Basically, a property $P_j, j = 1..m$ of a vitreous system featuring m properties is correlated to oxide composition $x_i, i = 1..n$ by the function f_j, such as:

$$P_j = f_j(x_1, x_2, ..., x_i, ..., x_n) \tag{1}$$

However, experimental and the in-depth study of the vitreous structure contradict the effectiveness of these models: it has been demonstrated that, in many cases, glasses with the same oxide composition can have different values of the properties [8, 9]. The reason is, oxide composition cannot determine, alone, the properties that can be influenced by the action of other parameters, such as, for example, melting temperature. Such parameter can change glass structural features that, in turn, will determine different glass properties for glasses of the same oxide composition [10, 11]. In these cases, glass properties cannot be defined by its oxide composition but by the percentage of p structural entities, $s_k, k = 1..p$:

$$P_j = g_j(s_1, s_2, ..., s_k, ..., s_p), \ \sum_{k=1}^{p} s_k = 1 \tag{2}$$

where g_j is the function defining property P_j with variables s_k. Such models can be found, for example, in [11-14].

According to the hierarchical structure of glasses, for different levels correspond different types of structural entities, therefore, Eq. (2) can be refined to:

$$P_j = g_j\left(s_1^{(r_1)}, s_2^{(r_2)}, ..., s_k^{(r_k)}, ..., s_p^{(r_p)}\right) \tag{3}$$

with $s_k^{(r_k)}$ being the entity s_k from the structural level $r_k, k = 1..p$. In such a case, types of entities can differ from an informational content viewpoint, i.e. they can belong to different structural levels. Due to that heterogenic size distribution, independent variables $s_k^{(r_k)}$ cannot be normalized.

By creating a complete inventory of glass properties, Goskel [15] revealed that properties correlate different with the local structure, i.e. groups of properties clearly depend on

short/medium/long range glass structure.

Trap and Stevels, quoted in [16], split the glass properties in 3 major groups:

- particles (atoms, ions) packing (structural compactness) related properties: density, refractive index, permittivity;

- entropy related properties: thermal expansion coefficient, surface tension etc.);

- structural relaxation properties: viscosity, dielectric loss.

By considering the structural features, Volf [16] grouped the properties in 4 classes. The first class contains properties – such as d, n and ε - reliant on, firstly, the arrangement of the particles in glass network; they are closely related to volume. Other properties belonging to that group – elastic modulus, microhardness, Poisson ratio – are influenced by other structural features such as bonds strength, polarizability of the ions. The second class includes temperature and mass, momentum or energy transfer related properties: diffusion coefficient and associated properties. The third class is made of properties related, mainly, to binding energy between cations and oxygen (the typical properties is the thermal expansion coefficient). The last class is made by only the chemical resistance.

Three levels can be used to describe the structural features of the glasses considered here:

- level 1 (r=1), represents the atomic level; structural entities are made of atoms (Na, Al, B, O) and their features (ion diameter/volume, molar volume, structural compactness C, polarizability, electronegativity etc.).

- level 2 (r=2), represents the atomic level; structural entities are made of elementary coordination polyhedra, such as: NaO_6, BO_3, BO_4, AlO_4, AlO_6 and their features (functional correlations between some physical properties of these glasses and types of structural entities are given in [6]);

- level 3 (r=3): structural entities are characterized by different types and sizes; altogether, they cannot be, till now, accurately defined;

- level 4 is not important because glasses studied here, under given preparation conditions, do not exhibit microphase separation phenomenon.

3.3. Parameters and equations

Optical properties were computed accordingly: reflection, R, Eq. (4), molar refractivity, R_m, Eq. (5), mass refractivity, R_M, Eq. (6), and specific refractivity, r, Eq. (7). [9]

$$R = 100 \left(\frac{n-1}{n+1} \right)^2 \qquad (4)$$

$$R_m = \frac{n^2-1}{n^2+2} \cdot \frac{\bar{M}}{d} \qquad (5)$$

$$R_M = \frac{n^2-1}{n^2+2} \cdot \frac{1}{d} \qquad (6)$$

$$r = \frac{n-1}{d} \qquad (7)$$

These optical properties will be correlated with three chemical and structural features at the first structural level (atomic): chemical composition, in x, %mol. Al_2O_3, molar volume, V_m and structural compactness, C (packing density) – see Eqs. (8-9).

$$V_m = \frac{\bar{M}}{d} = \frac{\sum_i x_i \cdot M_i}{d} \qquad (8)$$

$$C = \sum_i \sum_j \frac{x_{ij} \cdot V_{ij} \cdot N_A}{V_m} \qquad (9)$$

where: $\bar{M}$ is the average molar mass of the glass, kg/mol; d is the glass density, kg/m³; M_i molar mass of the ith oxide, kg/mol; V_{ij} – volume of the j ion in oxide i; x_{ij} – atomic fraction of the j ion in oxide i; N_A – Avogadro number (6.023x10²³ mol⁻¹).

By considering Eqs. (4)-(9) for current glasses, one can write:

$$V_m = \frac{66.95 + 0.4 \cdot x}{d(x)} \qquad (10)$$

$$C = \frac{(1756 + \quad \cdot x) \cdot d(x)}{(430 + 2 \cdot x) \cdot (66.95 + 0.4 \cdot x)} \qquad (11)$$

4. Results and discussions

Scholze [9], observed that, when decreasing Na_2O below 33% in the system Na_2O-B_2O_3, the molar volume recorded a slight increase, firstly, followed by a higher increase below 15% Na_2O. In the same system, partial replacement of Na_2O with Al_2O_3 has the following main consequences:

- an increase of the molar mass; apparently, of the density as well. As concerning density, the outcome, however, is opposite because molar volume of the Al_2O_3 is higher than Na_2O molar volume;

- AlO_4 resulted from $AlO_6 \rightarrow AlO_4$ conversion enters B-O-B network, thus inducing an increase of the molar volume.

These two effects work together to increase the molar volume with the increase of Al_2O_3 percentage and, therefore, a decrease of the density (see Table 1). Detailed information regarding the subject can be found in [17]. Also, the increase in Al_2O_3 content promotes the covalent character of the structure which, consequently, lead to the observed decrease of the refractive index.

4.1. Correlations optical properties-oxide composition

Light reflection depends on the angle of the incident beam with glass surface. A comparison between different glasses can be made by computing reflection R when the incident beam is perpendicular to glass surface, by considering only the refractive index of the glass, by Eq. (4).

In Figure 2 are plotted the values of R corresponding to the six studied glasses, according to their chemical composition, i.e. the content in Al_2O_3:
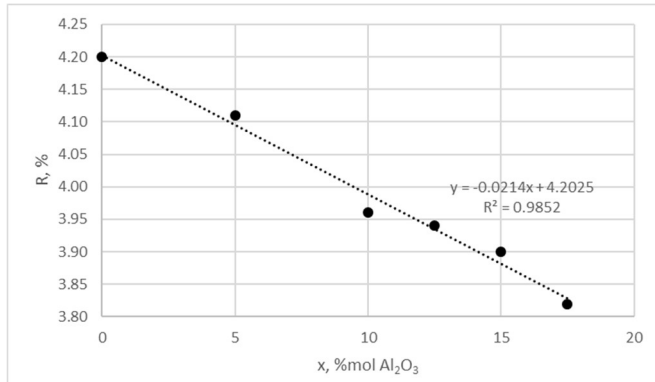
Fig. 2. - Light reflection vs. glass composition/*Coeficientul de reflexie în funcție de compoziția sticlei.*
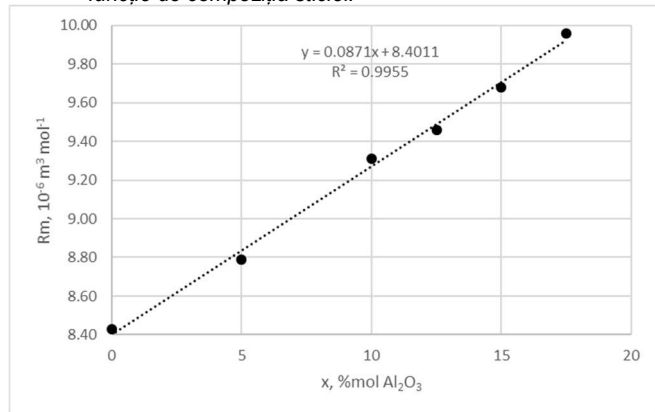

Fig. 3. - Molar refractivity vs. glass composition/*Refracția molară în funcție de compoziția sticlei.*
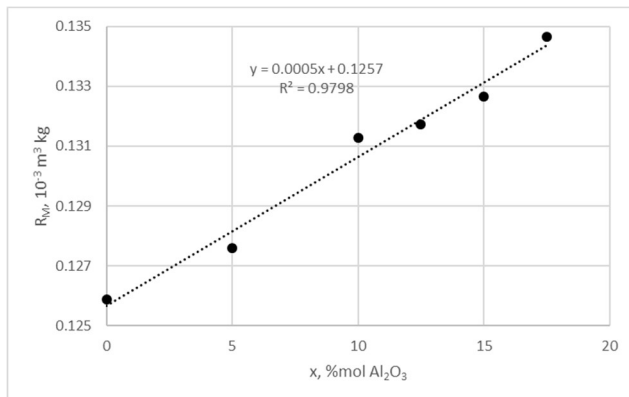

Fig. 4 - Mass refractivity vs. glass composition/*Refracția masică în funcție de compoziția sticlei.*
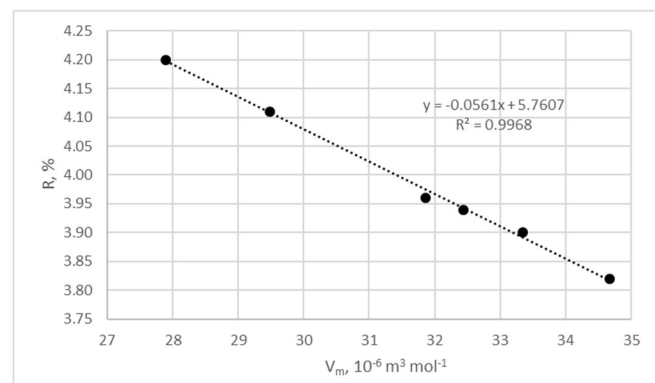

Fig. 5 - Light reflection vs. molar volume/*Coeficientul de reflexie în funcție de volumul molar.*

The analysis of Figure 2 reveals that, with the increase in Al_2O_3 content in glass, the light reflection diminishes with ~10% from 4.2% (the reference, borosilicate glass) to 3.8% for G5 glass. This behavior is to be expected as:

- the increase in x, %mol. Al_2O_3 will decrease the refractive index n (see Table 1);
- the derivative of the function $R=f(n)$ is strictly positive for $n>1$, therefore n and $R(n)$ will show the same descending trend from glass G0 to glass G5.

Isolated points can be identified within 10-15%mol. Al_2O_3 range that indicate a more accelerated structural transformation. This is confirmed by results published in [6]; according to [6], enhanced conversions $[AlO_6]\rightarrow[AlO_4]$ and $[BO_3]\rightarrow[BO_4]$ has been observed in this compositional domain.

For comparison reasons, reflection R is at about 4% for plain glass and 6.1% for flint [9].

Molar refractivity R_m can be defined as a measure of the strength electrons are bounded in an atomic system. This one depends mainly on the topology of the system. Consequently, R_m represents, also, a measure of the volume occupied by the atoms (ions) of the system within a mole of substance.

Molar refractivity R_m increases with content x, %mol. Al_2O_3 (see Fig. 3) due to:

- when x increases, refraction index n decreases while molar volume V_m increases in series G0-G5 (see Table 1 and [4]);
- even though in this series, the ratio $(n^2 - 1)/(n^2 + 2)$ decreases with about 5%, when x increases from 0 to 17.5, V_m increases substantially more (about 25%).

In Fig. 3 it was plotted the influence of x over R_m. The trend is almost linear, with some more important deviations within the range x = 10-15%, that indicate some structural changes typical to these glasses.

Mass refractivity R_M also increases with the content in Al_2O_3 since density decreases (in percentages) more substantially than decreases the ratio $(n^2 - 1)/(n^2 + 2)$. Also, both plots R_m and R_M vs x (see Fig. 4) show areas within the compositional range 10-15% Al_2O_3 that seem to be more important as regarding the R_M case.

Table 2

Specific refraction, r, vs. glass composition
Refracția specifică în funcție de compoziția sticlei

Glass code	x %mol Al_2O_3	r 10^{-3} m³·kg⁻¹
G0	0.0	0.215
G1	5.0	0.217
G2	10.0	0.223
G3	12.5	0.223
G4	15.0	0.225
G5	17.5	0.228

Statistical data of the correlations optical properties vs. structural compactness
Date statistice referitoare la corelația proprietăți optice-compactitate structurală

Property	Independent variable, x	Parameters		R^2
		m	n	
Glass reflection, R	Compactness, C	14.3570	2.1072	0.997
Molar refractivity, R_m	Compactness, C	-57.1580	16.7670	0.996
Masic refractivity, R_M	Compactness, C	-0.3277	0.1736	0.991

Specific refraction, *r*, records very small variations along with glasses composition (Table 2). With a fairly good approximation, it could be considered that in the compositional range 0-17.5%mol. Al$_2$O$_3$ the synthesized glasses have the same specific refraction $r = 0.222 \cdot 10^{-3}$ m^3/kg, maximal error comparing to values computed from experimental data *d* and *n* being ±2%.

4.2. Correlation optical property-molar volume
R against molar volume V_m is plotted in Figure 5, showing a similar behavior for the optical properties vs. composition, with a high correlation.

4.3. Correlations optical properties-structural compactness
The last analysis deals with correlations between optical properties $R/R_m/R_M$ and structural compactness of the glass, the last one being computed by Eq. (9). There were considered the following values for ionic radii: $r(Na^+) = 0.098$ nm, $r(B^{3+}) = 0.025$ nm, $r(Al^{3+}) = 0.057$ nm, $r(O^{2-}) = 0.140$ nm [10]. Almost linear ($y = mx+n$) plots of $R^2 \cong 1$ were extracted and the value of the coefficients *m* and *n* are given in Table 3.

5. Conclusions
Optical properties such as reflection, molar refractivity, mass refractivity and specific refractivity were computed, based on measured densities and refractive index on 6 glasses. The glasses that were synthesized have the compositions of (35-x)Na$_2$O·xAl$_2$O$_3$·65B$_2$O$_3$, *x* = 0-17% mol Al$_2$O$_3$.

Optical properties were evaluated in correlation to chemical composition, assessed by *x* = % mol Al$_2$O$_3$, molar volume V_m and structural compactness, *C*.

Correlations between optical properties and chemical composition, glass features at the first structural level (molar volume, V_m) and compactness, *C*, were drawn.

In this paper, V_m, V_M, *r* and *C* represents structural features associated to the fundamental (atomic) level.

The highest correlation was recorded for optical properties vs. compactness;

It was proved that structural features at the atomic level clearly controls functional properties at a macroscopic level.

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