Correlations Basicity-Deformation Properties in Borosilicate Vitreous Systems

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The glass properties in rigid and in melted form, mainly depend on the structural features of the vitreous system they belong to. Taking into account that basicity percentage, pb, is an indicator which “senses” the changes of the structural characteristics of oxide glasses, the properties of interest are expected to have an important correlation with the basicity percentage. In the present work, a series of such correlations between basicity percentage, experimentally determined, and measured values of some fixed points of viscosity, are emphasized for different glass compositions in the ternary system Na₂O-B₂O₃-SiO₂. The results and the obtained dependencies are compared to similar data from literature. In the second part of the work the correlation between the fragile/strong character of the glass forming melts and their basicity percentage is considered. For the evaluation of the fragile/strong character of glass forming melts an “s” index is proposed, which can be easily calculated by knowing the variation of viscosity with temperature.

Keywords: glass, fragility, basicity, correlation

Glass properties in rigid and in melted form, can be classified into two main categories: intrinsic and extrinsic. Intrinsic properties are those which depend mainly on the structural particularities of the vitreous system like density, refraction index, expansion coefficient, viscosity, etc.

In the case of the properties from the second category, although they present a certain degree of correlation with some structural characteristics, a more important influence present the extrinsic factors. It is the case of some properties like mechanical resistance or chemical stability.

Especially for the intrinsic properties, defining of some structural dependency parameters presents interest. These parameters can be: electrostatic field intensity of the component cations, electronegativity, electronic polarizability of the oxygen ion (in oxide glasses), energy of the cation-oxygen chemical bonds, etc. Another quantity that is a complex structural parameter is the basicity percentage, pb. It can be calculated [1] or experimentally determined [2] by spectroscopic measurements (for oxide glasses).

Through its definition, the basicity percentage, pb, takes into account a series of structural characteristics such as bond’s ionicity percentage, coordination number, the pb correlating in fact with all the structural characteristics at an atomic level (electrostatic field’s strength, electronegativity, oxygen’s electronic polarizability, oxidation number, bonding energies etc.) [3].

From the high statistical correlation degree between pb and various structural parameters used in time to elaborate atomistic theories regarding the genesis of the vitreous state results that pb values can represent a measurement of the acid-base character for the vitreous oxide systems.

Taking into account that the basicity percentage is an indicator which “senses” the modification of the structural characteristics of oxide glasses, it is expected that the properties of interest (temperatures corresponding to structural transformations, thermal expansion coefficient, refraction index, viscosity etc.) to have an important correlation with the basicity percentage [4].

In the present work, a series of such correlations between the basicity percentage, experimentally determined, and measured values of some fixed viscosity points are emphasized, for glasses of different compositions obtained in the Na₂O – B₂O₃ – SiO₂ ternary system.

From fundamental point of view, this system presents interest in relation to its structure that is not fully elucidated. At the same time, the system considered is the basis of obtaining an important class of glasses, namely borosilicate glasses, which have multiple uses in various fields.

The obtained results and dependencies are compared to similar data from literature [5].

In the second part of the work, the fragile/strong character [6-8] issue for glass forming melts and correlation with their basicity percentage is treated. At the same time it is shown that at nano level the structure of the melts for the silicate glasses is heterogeneous, which implies a rough profile for the distribution of the free energy values. This reality implies a fragile character more or less rough of these melts.

For the evaluation of the fragile/strong character of the silicate glass forming melts an “s” index that can be easily calculated knowing viscosity variation with temperature, is proposed.

The glass basicity is measured through the basicity percentage indicator, and through the number of unbonded oxygen atoms compared to the Si atom, respectively.

Experimental part
Three sodium borosilicate glasses were synthesized with gravimetric compositions presented in table 1.

The traditional melting method was used at temperatures between 1300-1500°C, the melting taking place in an electric oven with superkanthal, in platinum crucibles using as raw materials: quartz (>99.5% SiO₂), boric acid and Na₂CO₃ of analytic grade. H₃BO₃ and Na₂CO₃ were used in excess to avoid losses due to volatilization. The casting took place in graphite die obtaining prismatic samples which were annealed at a temperature close to
the vitreous transition temperature $T_g$, corresponding to each synthesized glasses. The chemical analysis for the obtained glasses emphasized a composition close to that theoretically proposed.

Simultaneously with each of the synthesized glasses, another glass of the same composition was melted but with 0.1% atomic Cu, used as sensor in experimentally determining basicity percentage, in accordance with the quantitative method proposed [2].

Using a spectrophotometer SHIMADZU UV-VIS with 2 beams, the extinctions (-logT) were obtained for each of the sodium borosilicate glass samples with 0.1% at. Cu and compared to the glass samples with the same composition but without ion sensor. The thermal expansion curve for the synthesized glasses was obtained using a dilatometer Linseis L75 assisted by computer and the structural transformation temperatures and the linear thermal expansion coefficient ($\alpha_{20^\circ}$) were determined.

An amplification factor A=1000 was used and the heating rate of the oven was 4°C / min.

Results and discussions
The experimental method of determining the glass basicity percentage proposed [2] uses as measure of basicity the minimal energy expressed as wavenumber, to which the absorption through charge transfer of the 3d ion sensors of Cu$^{2+}$, respectively, takes place. In order to exemplify, in figure 1, the Cu$^{2+}$ UV absorption spectrum is presented for one of the synthesized sodium borosilicate glasses.

Thus, a dependency of pB with the wavenumber \( \nu \) (cm$^{-1}$) was obtained:

\[
pB = 151 - 0.00259 \cdot \nu; \quad (1)
\]

Using the wavelength values \( \lambda \) and the wavenumbers \( \nu \) obtained for the absorption of Cu$^{2+}$, respectively, in the case of the three synthesized sodium borosilicate glass pairs (with and without sensor) and using relation (1), the experimental basicity percentage was determined for the three ternary glasses. The results are shown in table 2.

For the ternary compositions of the Na$_2$O-B$_2$O$_3$-SiO$_2$ system taken from literature, the theoretical basicity percentage pB was calculated with relation:

\[
pB = \sum \frac{c_i}{1+P_i} ; \quad (2)
\]

in which: \( c_i \) is the gravimetric fraction of the \( i \)-th oxide, and pB, the basicity percentage of the \( i \)-th oxide determined with [1]:

\[
\log pB_i = 1.9(\text{NC})^{0.02} - 0.023P_i/\text{NC} \quad (3)
\]

where: NC – is the coordination number of the cation related to oxygen, \( P_i \) - the ionization potential of the cation for the given valence state.

For calculating the theoretical basicity percentage, the boron tetracoordinated fraction (N$_4$) obtained from the Bray diagram [9] was taken into account, according to the molar fractions R=Na$_2$O/B$_2$O$_3$ and K=SiO$_2$/B$_2$O$_3$, for each of the considered compositions.

The values of the vitreous transition temperatures, $T_g$, as well as the values of the dilatometric softening temperature, $M_g$, experimentally determined for the synthesized glasses, are graphically represented in figures 2-3 together with the $T_g$ and $M_g$ values for the glasses taken from literature, in accordance with the experimental and theoretical basicity percentage for the considered glasses, respectively.
Fig. 2-3 Dependency between the vitreous transition temperature, \( T_g \), and the dilatometric softening temperature \( M_g \), respectively and the basicity percentage, \( p_B \), for the considered glasses.

Table 3

<table>
<thead>
<tr>
<th>No. glass</th>
<th>( p_B ) (%)</th>
<th>( T_g ) (°C)</th>
<th>( \ln \eta )</th>
<th>Coefficients</th>
<th>VFT equation</th>
<th>( s ) [0,1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60.69</td>
<td>533</td>
<td>13.30</td>
<td>(-2.90)</td>
<td>(-2.90+3861.53/\left(394.65\right))</td>
<td>0.4477</td>
</tr>
<tr>
<td></td>
<td></td>
<td>800</td>
<td>4.74</td>
<td>(3861.53)</td>
<td></td>
<td>(-2.90+3861.53/\left(394.65\right))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>949</td>
<td>3.00</td>
<td>(294.65)</td>
<td></td>
<td>(-2.90+3861.53/\left(394.65\right))</td>
</tr>
<tr>
<td>2</td>
<td>56.61</td>
<td>574</td>
<td>13.3</td>
<td>(-4.75)</td>
<td>(-4.75+5600.56/\left(263.76\right))</td>
<td>0.5568</td>
</tr>
<tr>
<td></td>
<td></td>
<td>671</td>
<td>9.00</td>
<td>(5600.56)</td>
<td></td>
<td>(-4.75+5600.56/\left(263.76\right))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>900</td>
<td>4.05</td>
<td>(263.76)</td>
<td></td>
<td>(-4.75+5600.56/\left(263.76\right))</td>
</tr>
<tr>
<td>3</td>
<td>61.99</td>
<td>510</td>
<td>13.3</td>
<td>(-2.34)</td>
<td>(-2.34+3428.15/\left(290.91\right))</td>
<td>0.4265</td>
</tr>
<tr>
<td></td>
<td></td>
<td>831</td>
<td>4.00</td>
<td>(3428.15)</td>
<td></td>
<td>(-2.34+3428.15/\left(290.91\right))</td>
</tr>
<tr>
<td></td>
<td></td>
<td>952</td>
<td>3.00</td>
<td>(290.91)</td>
<td></td>
<td>(-2.34+3428.15/\left(290.91\right))</td>
</tr>
</tbody>
</table>

Thus, it can be observed a linear decrease of the vitreous transition temperature and of the dilatometric softening temperature with the increase of the basicity, \( p_B \) and with the increase of the sodium oxide content, for the presented compositions, respectively. As \( T_g \) and \( M_g \) are fixed viscosity points, the explanation of their decrease consists in the increase of the number of unbounded oxygen atoms related to the Si atom, hence the formation of weaker bonds once new amount of modifying oxide is introduced. At the same time, it is known that the sodium oxide presents a greater basicity (\( p_B \)) than that of the forming oxides to be replaced in the glass structure. As a consequence, a decrease of the polymerization degree of the vitreous structure takes place which finally leads to smaller and smaller values of the vitreous transition temperature and of the dilatometric softening temperature with the increase of the basicity percentage.

It must be outlined the fact that the values of the properties obtained for the three sodium borosilicate glasses experimentally synthesized are situated well in the general trend given by the values of the properties for the ternary compositions taken from literature, which are more numerous.

For the vitreous melts, the “strong” or “fragile” character is emphasized through the way viscosity varies with temperature. Thus, in coordinates \( \ln \eta/\theta \) \((\theta = T/T_g)\), where \( T \) is the temperature of the melt and \( T_g \) is the vitreous transition temperature, the graph presents a linear form for the “strong” melts; in cases where a bent is present, it reflects the more pronounced “fragile” character of melts [6,7].

Phenomenologically speaking, the “strong” melts have a viscosity with temperature which is well described by the Arrhenius equation. By contrast, “fragile” melts have a viscosity variation with temperature described by the Vogel-Fulcher-Tammann (VFT) equation.

According to the polymer theory, silicate glasses present a structure that is formed of more types of structural entities. Effective chemical composition, number, dimension and percentage of these structural species depend on the oxide composition of the glass and on the “thermal history”. But this particular distribution of the structural entities imprints a nanoheterogenous character to the glass melts. Consequently, these systems are characterized by a very irregular energetic profile, and that imprints a “fragile” character more or less pronounced.

For comparison, the SiO\(_2\) melt, which has a pronounced structural uniformity, presents a great “strong” behavior.

Based on some semi-empirical theoretical assumptions, the evaluation of the “strong” character of vitreous melts can be done with the help of a coefficient “\( s \)”, defined as:

\[
s = \frac{(1-T/T_g)^2}{(1-0.6 \cdot T/T_g)^2}
\]

where, \( T \) is a coefficient that appears in the Vogel-Fulcher-Tammann relation.

On the basis of the experimental results obtained for the vitreous transition temperature, \( T_g \) (\( \ln \eta = 13.3 \)), and with the help of two more temperature values corresponding to smaller viscosities, taken from literature [5] for glasses with identical compositions or very close to each of the three synthesized glasses of interest, the A, B and \( T_0 \) coefficients corresponding to the Vogel-Fulcher-Tammann equation could be calculated for each composition. With these values, the “\( s \)” indices, assigned...
by relation (4), were calculated. The data are presented in table 3. The dependence of the “strong” character on the basicity percentage is given in figure 4.

As expected, as the glass basicity increases, the “s” index decreases, and therefore the fragility increases. The explanation consists in the fact that with the increase of basicity the nanoheterogenous character becomes more pronounced, which implies eventually an energetic profile with greater fluctuations. Finally it results an increase in the fragility of the melts.

Conclusions

Three glasses were synthesized in the Na₂O–B₂O₃–SiO₂ ternary system for which experimental basicity and structural transformation temperatures were determined. The good correlation between Tᵣ and pB, respectively, confirms the fact that the basicity percentage is for the vitreous systems a structural parameter that “senses” the structural modifications that take place with the variation of the chemical composition. At the same time, based on the viscosity data and using the Vogel-Fulcher-Tammann relations, the strong character “s” was determined for the three glasses. The results show that as the glass basicity increases, the “s” index decreases, the glasses becoming more and more fragile.

References

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