Optical and Photonic Glasses

Lecture 6:
Structures of Glass II – Glass Families

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Designations for **modified silicate glasses**

Example of alkaline-earth silicates (MO.SiO$_2$, in mol%):

<table>
<thead>
<tr>
<th>example</th>
<th>designation</th>
<th>net. dimens.</th>
<th># BO/tetr.</th>
<th>symbol</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 % MO  → SiO$_2$</td>
<td>(silica)</td>
<td>3-D</td>
<td>(4 BO/tetr.)</td>
<td>Q$_4$</td>
</tr>
<tr>
<td>33 % MO → CaO.2 SiO$_2$</td>
<td>(disilicate)</td>
<td>2-D</td>
<td>(3 BO/tetr.)</td>
<td>Q$_3$</td>
</tr>
<tr>
<td>50 % MO → CaO.SiO$_2$</td>
<td>(metasilicate)</td>
<td>1-D</td>
<td>(2 BO/tetr.)</td>
<td>Q$_2$</td>
</tr>
<tr>
<td>60 % MO → 3 CaO.2 SiO$_2$</td>
<td>(pyrosilicate)</td>
<td>dimers</td>
<td>(1 BO/tetr.)</td>
<td>Q$_1$</td>
</tr>
<tr>
<td>66 % MO → 2 CaO.SiO$_2$</td>
<td>(orthosilicate)</td>
<td>monomers</td>
<td>(0 BO/tetr.)</td>
<td>Q$_0$</td>
</tr>
</tbody>
</table>
Modified silicate glasses

A) Fraction of NBO atoms ($f_{NBO}$)

molar basis: $20 \text{Na}_2\text{O} \cdot 80 \text{SiO}_2 = \text{Na}_2\text{Si}_4\text{O}_9$

$1 \text{Na}^+ \Rightarrow 1 \text{NBO}^-$ \hspace{1cm} (1 $\text{Ca}^{2+} \Rightarrow 2 \text{NBO}^-$)

\[
f_{NBO} = \frac{2}{9} = 22\% \ (0.22)
\]

B) Average number, $y$, of corners shared, or BO, per tetrahedron (for particular compositions, this coincides with the subscript $n$ in $Q_n$ symbols):

\[
y = 6 - \left(\frac{200}{\text{mol}\% \text{SiO}_2}\right) \quad \text{(only for tetrahedral silicates)}
\]

Example: in a disilicate glass, the basic structural unit is a $Q_3$ “tetrahedron” (strictly speaking, a trigonal pyramid, where the Si-O bond is shorter than in Si-O-Si bonds), possessing $(3 \text{BO} + 1 \text{NBO})$ species and a total of 2.5 (net) oxygen atoms. Hence its chemical formula:

\[
\text{Na}_2\text{O} \cdot 2 \text{SiO}_2 = \text{Na}_2\text{Si}_2\text{O}_5 \quad \text{where} \quad \text{O/Si} = 5/2 = 2.5
\]
This is a 2-D representation of the *modified random network* model of G.N. Greaves et al. (The structure of Non-Crystalline Materials, Taylor & Francis, 1983) for a modified silicate glass.

- Si
- Na
- O
- O

In this model, there are *channels* along which the *modifier ions* (Na\(^+\), in this case) are preferentially located, corresponding to a certain extent of *phase separation* in the modified glass.
Alkali aluminosilicate glasses: 4- and 6-fold coordinated Al

\[
\text{Al}_2\text{O}_3 / \text{M}_2\text{O} < 1 \Rightarrow \text{CN}_{\text{Al}} = 4
\]
(excess negative charge of \([\text{AlO}_4]\) group satisfied by \(\text{M}^+\) ion)

\[
\text{Al}_2\text{O}_3 / \text{M}_2\text{O} = 1 \Rightarrow \text{CN}_{\text{Al}} = 4
\]
(network \textit{former}) and no NBO present (adding one \text{Al}^{3+} to an alkali silicate removes one NBO)

\[
\text{Al}_2\text{O}_3 / \text{M}_2\text{O} > 1 \Rightarrow \text{excess Al}^{3+}\text{ are modifiers, with CN}_{\text{Al}} = 6
\]

(Presumably, a modifying \text{Al}^{3+} ion, with octahedral coordination, will have its charge compensated by 3 singly charged NBO ions).

Suggested structure of an alkali aluminosilicate glass with \text{Al}^{3+} as a network modifier showing octahedrally coordinated \text{Al}^{3+}.

Alkali aluminosilicate glasses: 4-fold coordinated Al

even for Al$_2$O$_3$ / M$_2$O > 1

Tetrahedrally coordinated Al$^{3+}$ in tricluster arrangements (a) and (b) according to Lacy. Note that (c) is equivalent to (a).

(E.D. Lacy, 1963)

X-ray photoemission (or photoelectron) spectroscopy (XPS)

XPS is one of the best available experimental tools for the identification and quantitative determination of NBO species in oxide glasses.

\[ n = 1 \]

\[ \text{incident X-ray (hv)} \]

\[ \text{de-excitation leaves a positively charged oxygen ion} \]

\[ n = 2 \]

\[ \text{ejected O 1s photoelectron} \]

\[ \text{Photoelectron: } \text{BE} = \text{hv} - \text{KE} \quad (\text{e.g., } O_{1s} : \text{BE} \sim 532 \text{ eV}) \]

\[ \text{De-excitation energy: (1) X-ray photon (XRF); (2) secondary Auger electron (KLL), leaving a doubly positively charged oxygen ion.} \]
High resolution O1s XPS spectra of silica and sodium silicate glasses. (The areas under the low and high BE peaks, separated by ~ 2 eV, are proportional to the NBO/BO atomic ratio).

O1s spectra of the sodium silicate glasses (kinetic energy scale relative to the energy of the BO's).

XPS may be applied to non-oxide glasses as well. E.g., ZrF₄-based glasses have *bridging* and *non-bridging* fluorine ions, but with a smaller difference in BE.
Lead silicate and lead borate glasses may contain more than 90 weight% PbO. In such glasses, it is believed that Pb\textsuperscript{2+} cations assume a network-forming role, either coordinated by two oxygen ions (fig. (a)) or by four, forming [PbO\textsubscript{4}] pyramids (fig. (b)).


Structure of lead silicate glasses showing (a) two-coordinated Pb, (b) tetrahedrally coordinated Pb. (After Mydler et al. [22]. Redrawn with permission of the Society of Glass Technology.)
The structure of pure \( \text{B}_2\text{O}_3 \) glass, as evidenced from detailed NMR and Raman spectroscopy studies and confirmed by XRD, appears to have the so-called boroxol ring as the fundamental structural unit, formed by three B atoms, each surrounded by three nearest neighbor BO atoms.

Configuration of the boroxol ring.


As a modifier such as \( \text{Na}_2\text{O} \) is progressively added to \( \text{B}_2\text{O}_3 \), an increasing number of B atoms go into tetrahedral rather than triangular coordination. This has significant consequences, in particular a clear minimum in the thermal expansion coefficient vs. \([\text{Na}_2\text{O}]\) curve, usually designated as the boron oxide anomaly.
\( \text{P}_2\text{O}_5 \) is a glass-forming compound. The coordination of P in pure \( \text{P}_2\text{O}_5 \) glass is believed to be similar to that found in \( \text{PO}_4 \) and \( \text{P}_4\text{O}_{10} \) molecules (figs. (a) and (b)), consisting of three single bonds and a double P=O bond. This has a special type of NBO, corresponding to a terminal bond shorter than a normal P-O- terminal bond.

One well known type of modified phosphate glass is the *metaphosphate* glass composition, where the basic structural units are chains. In the case of sodium metaphosphate (NaPO₃) glass, the structural unit may be represented as follows:

\[
\text{O}^- \text{Na}^+ \text{O} \\
\vdots \quad \quad \quad \quad \quad \quad \vdots \\
\text{O} \quad \text{P} \quad \text{O} \quad \text{P} \quad \text{O} \\
\vdots \quad \quad \quad \quad \quad \quad \vdots \\
\text{O} \quad \text{Na}^+ \text{O}^- \\
\]

The out-of-chain P-O bonds have a character in-between a single and a double bond. Alternatively, this situation might be depicted by means of a regular single P-O⁻ bond and double P=O bond on opposite sides of each P atom. The figure includes examples of both descriptions.
Halide glasses such as the ZrF$_4$-based ones are more ionic than oxide glasses and the network-forming cation, Zr$^{4+}$, has higher coordinations than those predicted by Zachariasen’s rules (CN$_{Zr}$ has been found to be between ~ 6 - 8).