Optical and Photonic Glasses

Lecture 6:

Structures of Glass II – Glass Families

Professor Rui Almeida

International Materials Institute
For New Functionality in Glass
Lehigh University

Designations for **modified silicate glasses**

Example of alkaline-earth silicates ($MO.SiO_2$, in mol%):

	example	designation	net. dimens.	# BO/tetr.	symbol
0 % MO →	SiO_2	(silica)	3-D	(4 BO/tetr.)	Q_4
33 % MO →	$CaO.2\ SiO_2$	(disilicate)	2-D	(3 BO/tetr.)	Q_3
50 % MO →	$CaO.SiO_2$	(metasilicate)	1-D	(2 BO/tetr.)	Q_2
60 % MO →	$3\ CaO.2\ SiO_2$	(pyrosilicate)	dimers	(1 BO/tetr.)	Q_1
66 % MO →	$2\ CaO.SiO_2$	(orthosilicate)	monomers	(0 BO/tetr.)	Q_o

Modified silicate glasses

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

molar basis: $20\ Na_2O.80\ SiO_2 = Na_2Si_4O_9$

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

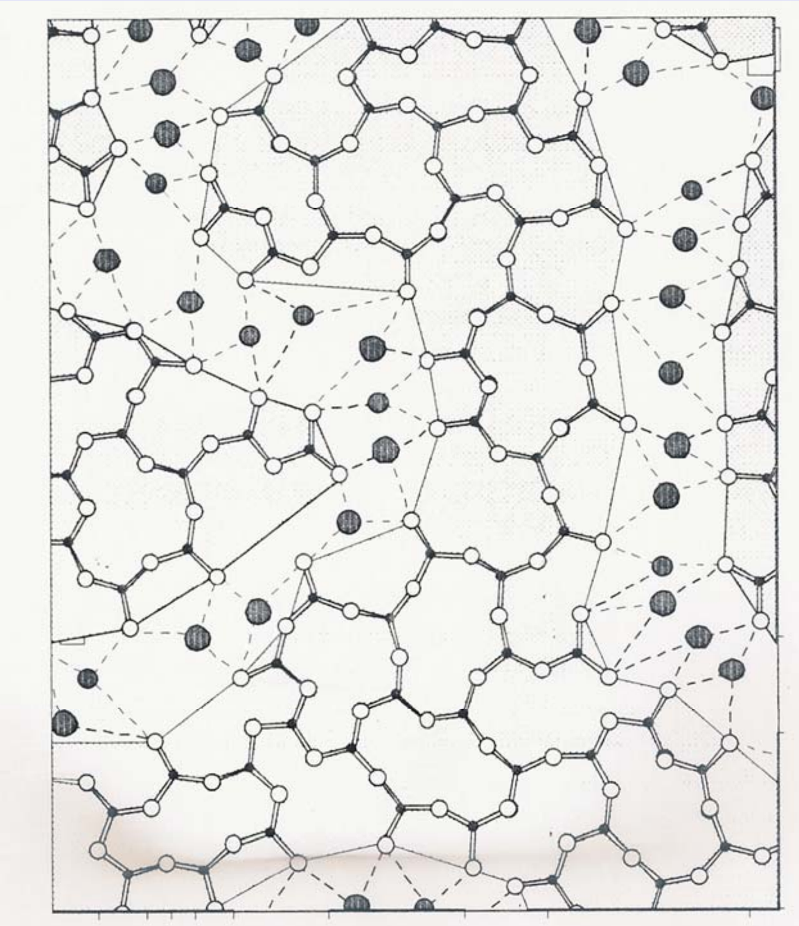
$$f_{NBO} = 2/9 = 22\% \quad (0.22)$$

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

$$y = 6 - (200 / \text{mol\% } SiO_2) \qquad \text{(only for tetrahedral silicates)}$$

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

$$Na_2O.2\ SiO_2 = Na_2Si_2O_5 \qquad \text{where } O/Si = 5/2 = 2.5$$



This is a 2-D representation of the *modified random network* model of G.N. Greaves at al. (The structure of Non-Crystalline Materials, Taylor & Francis, 1983) for a modified silicate glass

- Si

● Na

O O

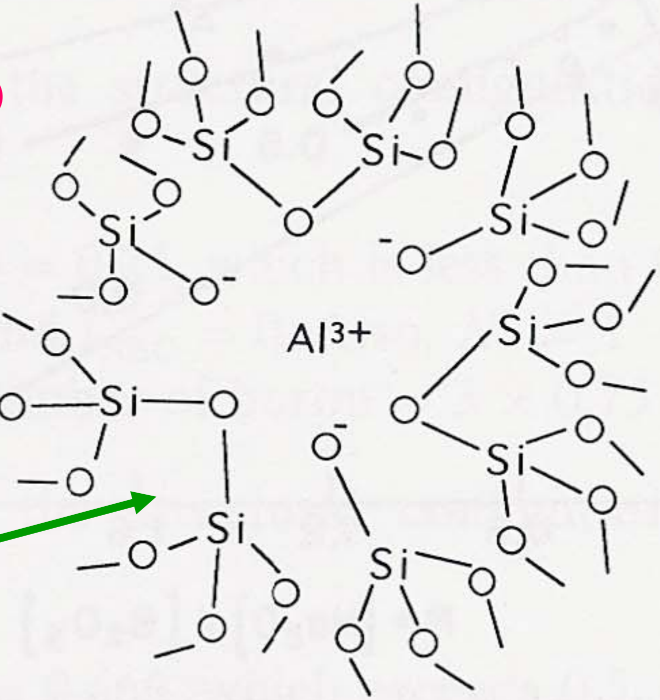
In this model, there are **channels** along which the **modifier ions** (Na$^+$, in this case) are preferentially located, corresponding to a certain extent of *phase separation* in the modified glass.

Alkali aluminosilicate glasses: 4- and 6-fold coordinated Al

$Al_2O_3 / M_2O < 1 \Rightarrow CN_{Al} = 4$ (excess negative charge of $[AlO_4]$ group satisfied by M^+ ion)

$Al_2O_3 / M_2O = 1 \Rightarrow CN_{Al} = 4$ (network **former**) and no NBO present (adding one Al^{3+} to an alkali silicate removes one NBO)

$Al_2O_3 / M_2O > 1 \Rightarrow$ excess Al^{3+} are **modifiers**, with $CN_{Al} = 6$



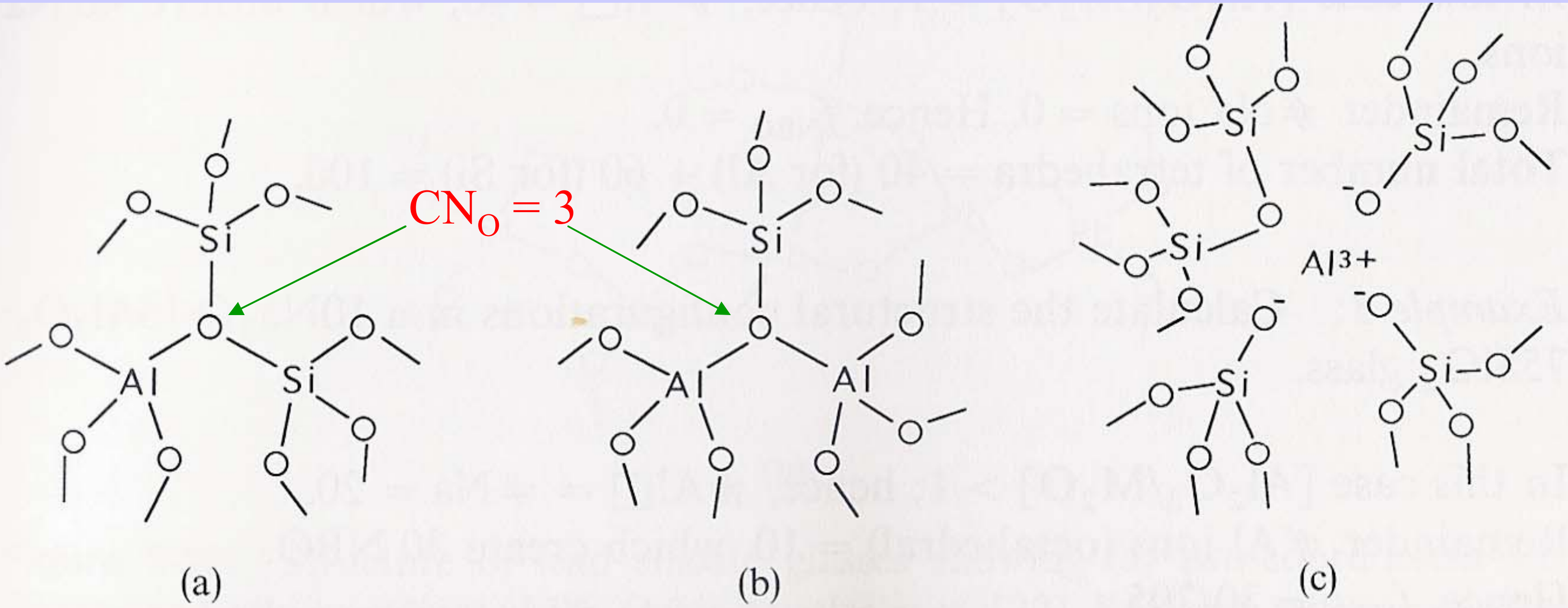
(Presumably, a modifying Al^{3+} ion, with octahedral coordination, will have its charge compensated by 3 singly charged NBO ions).

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

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

Alkali aluminosilicate glasses: 4-fold coordinated Al

even for Al_2O_3 / $M_2O > 1$



(a) (b) (c)

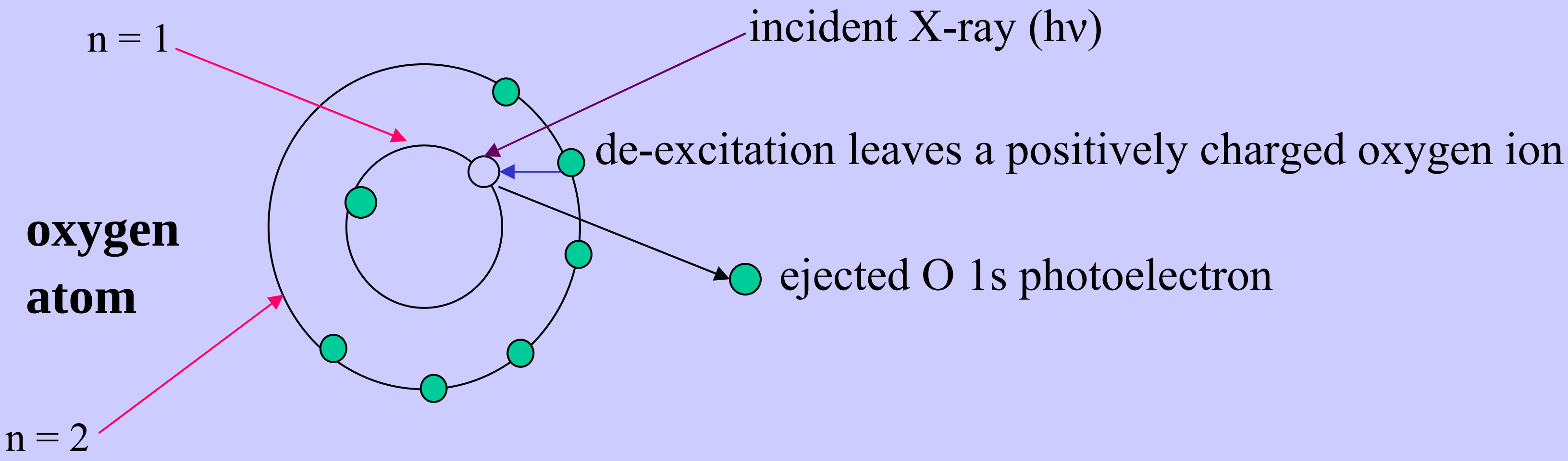
Tetrahedrally coordinated Al^{3+} in tricluster arrangements (a) and (b) according to Lacy. Note that (c) is equivalent to (a).

(E.D. Lacy, 1963)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

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

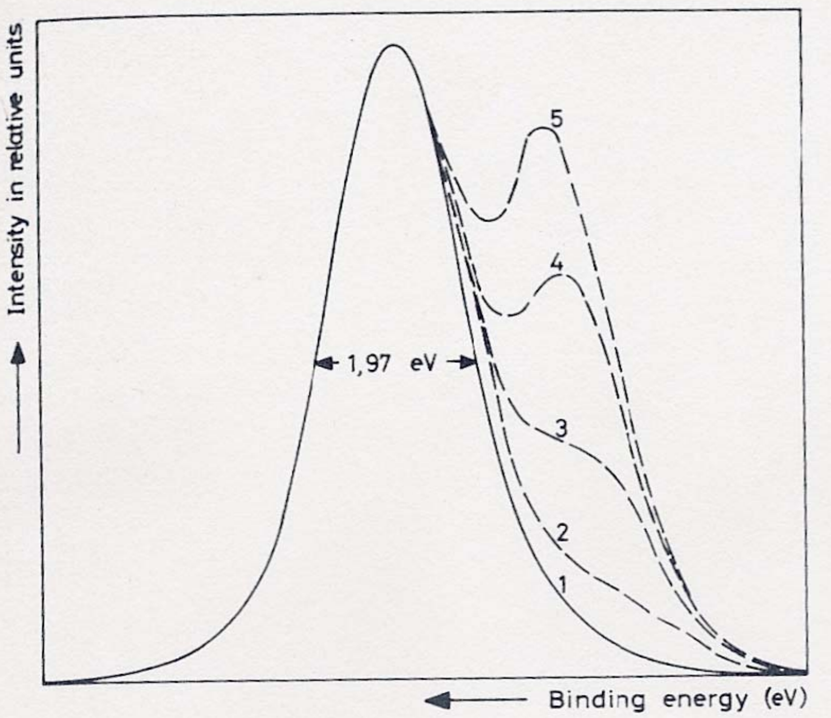
XPS is one of the best available experimental tools for the identification and quantitative determination of NBO species in oxide glasses.



Photoelectron: BE = hν – KE (e.g., O_{1s} : BE ~ 532 eV)

De-excitation energy: (1) X-ray photon (XRF); (2) secondary Auger electron (KLL), leaving a doubly positively charged oxygen ion.

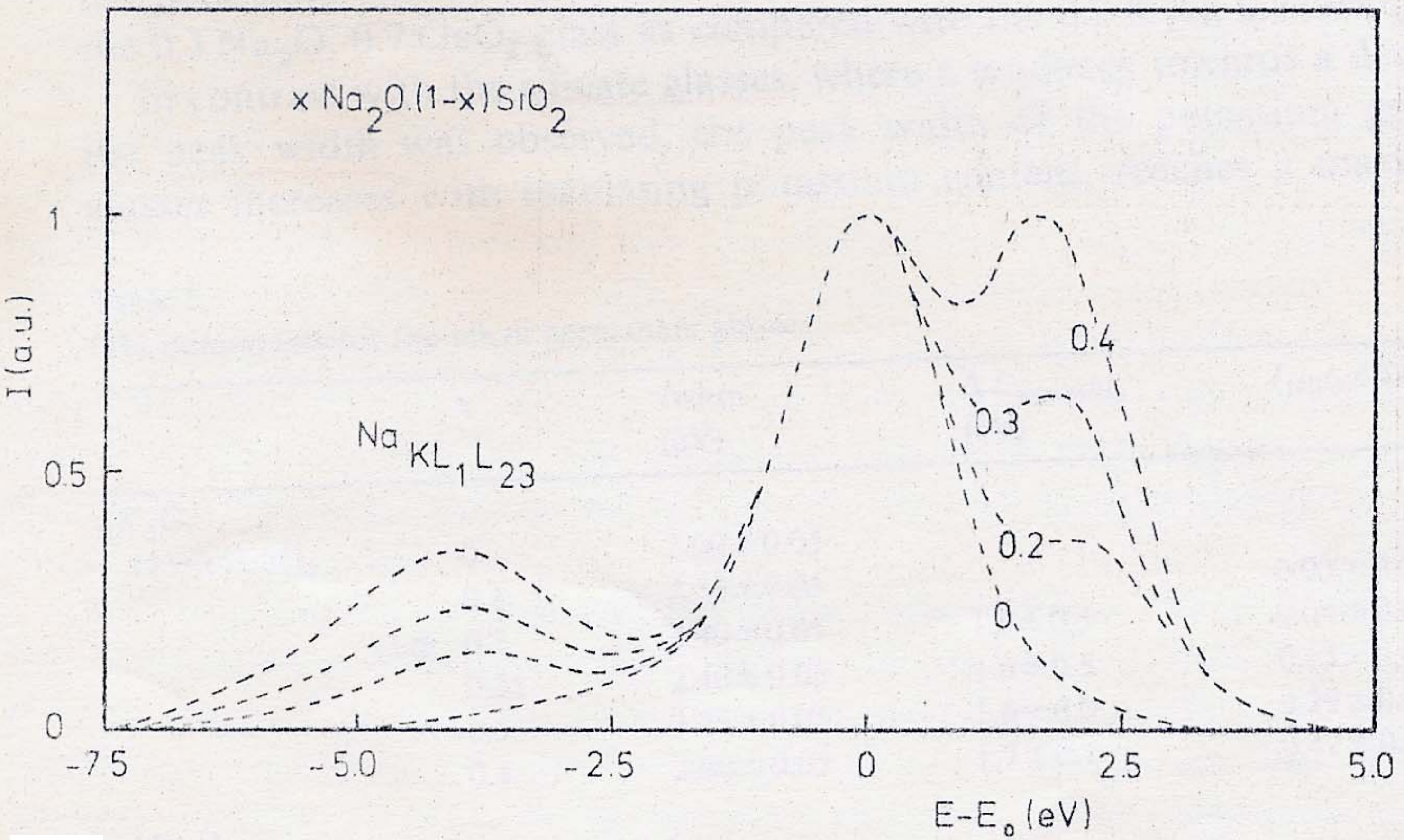
High resolution O1s XPS spectra of silica and sodium silicate glasses. (The areas under the low and high BE peaks, separated by ~ 2 eV, are proportional to the NBO/BO atomic ratio).



O 1s-spectra of silica glasses and sodium silicate glasses.

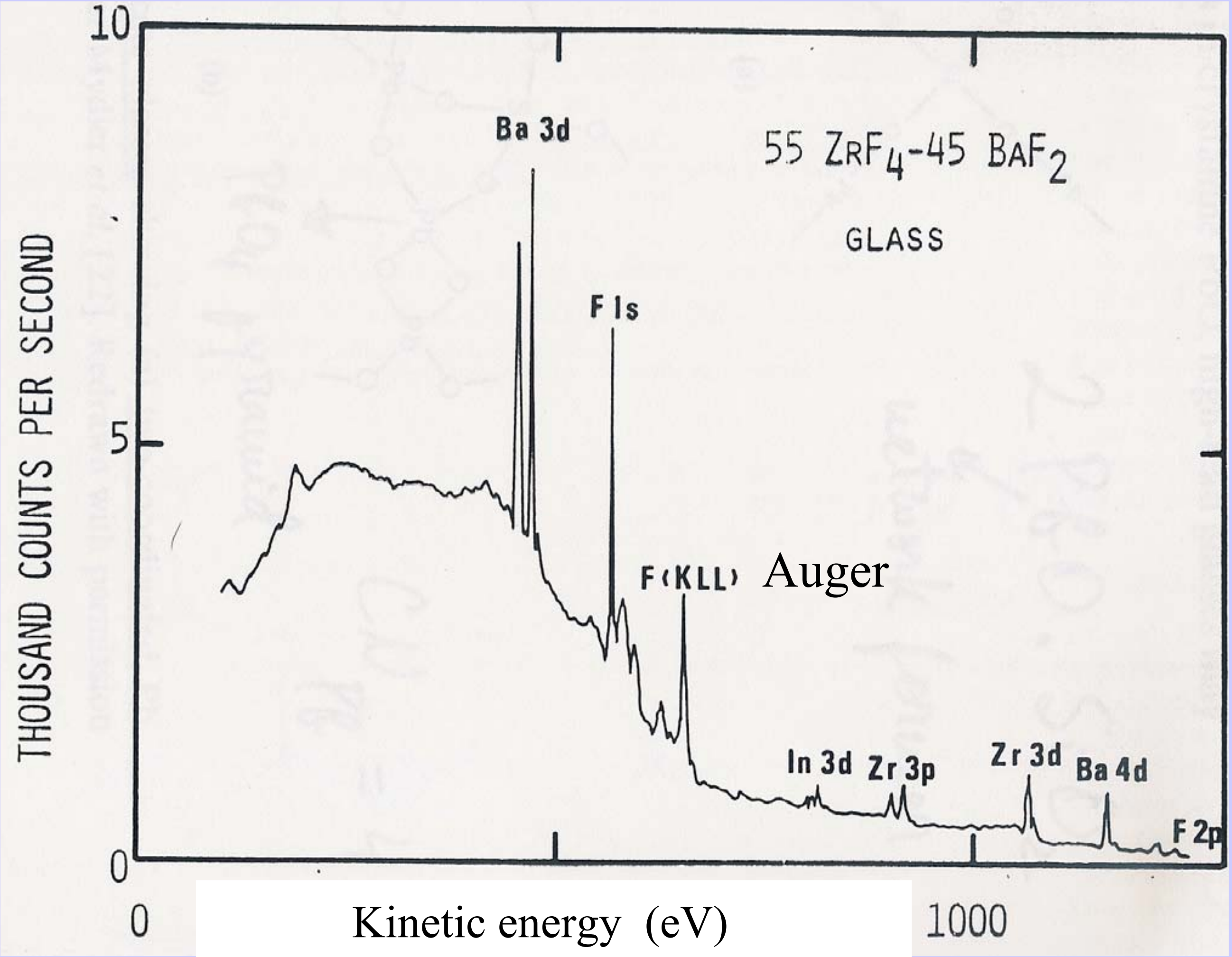
1: Suprasil W, Suprasil, Infrasil
2: 9 wt.-% Na_2O
3: 20 wt.-% Na_2O
4: 30 wt.-% Na_2O
5: 40 wt.-% Na_2O

(Adapted from: R. Bruckner et al., Jap. J. Appl. Phys.,1978)



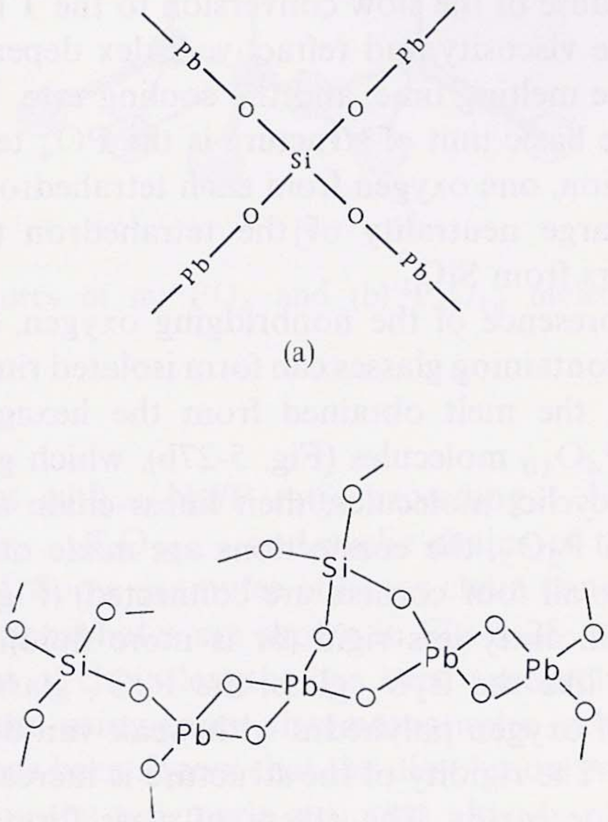
[redacted] O1s spectra of the sodium silicate glasses (kinetic energy scale relative to the energy of the BO's).

(Adapted from: B.M.J. Smets and T.P.A. Lommen, J. Non-Cryst. Solids, 1981)



XPS may be applied to non-oxide glasses as well. E.g., ZrF_4-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^{2+} cations assume a network-forming role, either coordinated by two oxygen ions (fig. (a)) or by four, forming $[PbO_4]$ pyramids (fig. (b)).



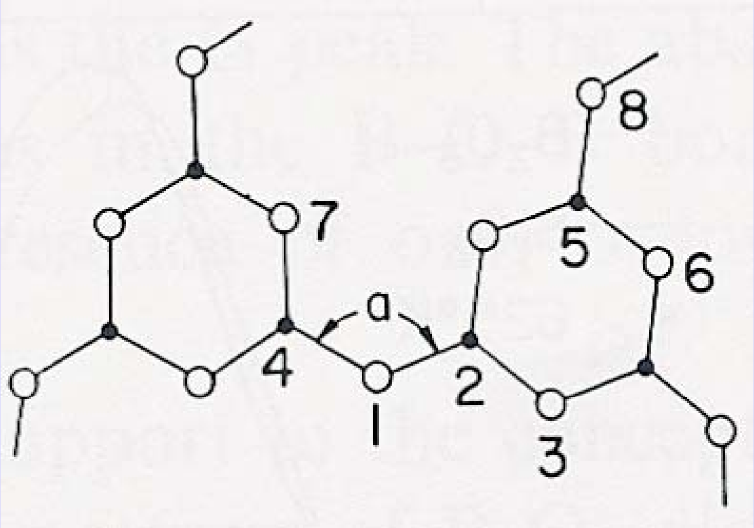
(a)

(b)

[redacted] 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.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

The structure of pure **B_2O_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.

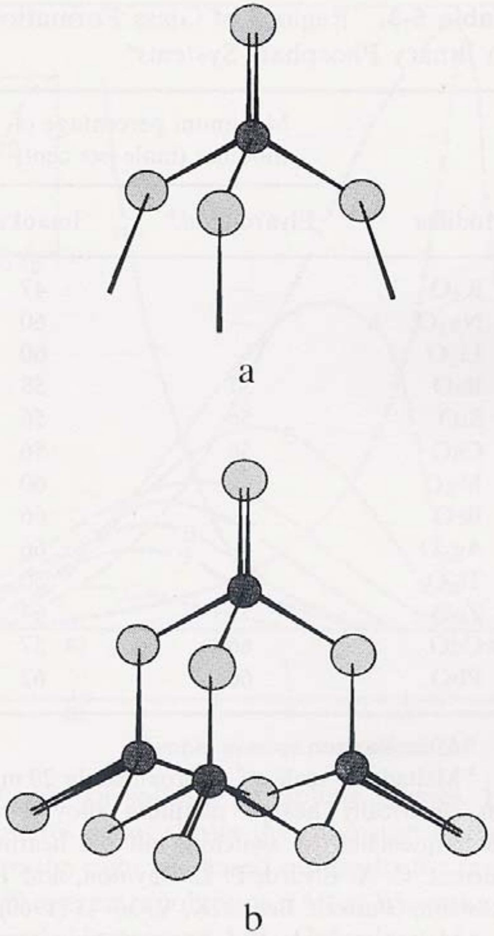


Configuration of the boroxol ring.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

As a modifier such as Na_2O is progressively added to B_2O_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. [Na_2O] curve, usually designated as the *boron oxide anomaly*.

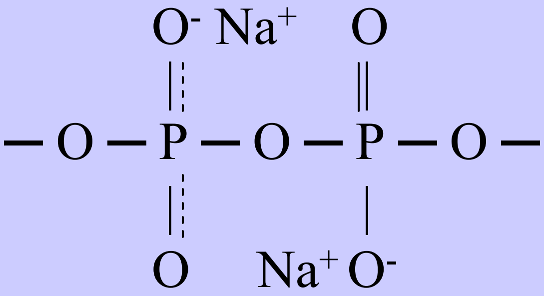
P_2O_5 is a glass-forming compound. The coordination of P in pure **P_2O_5 glass** is believed to be similar to that found in PO_4 and P_4O_{10} molecules (figs. (a) and (b)), consisting of three single bonds and a double P=O bond. This has a special type of NBO, corresponding to a terminal bond shorter than a normal $P\text{-}O^-$ terminal bond.



Structures of (a) PO_4 and (b) P_4O_{10} molecules. Darker-shaded circles represent P.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

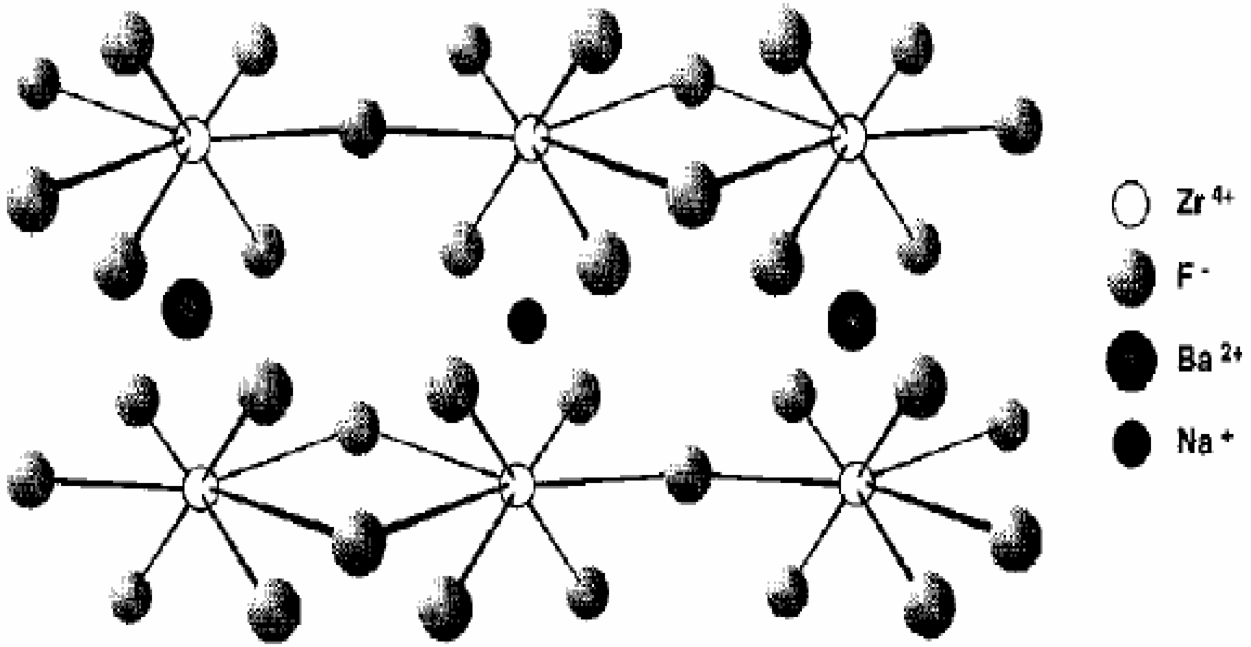
One well known type of modified phosphate glass is the *metaphosphate* glass composition, where the basic structural units are chains. In the case of sodium metaphosphate ($NaPO_3$) glass, the structural unit may be represented as follows:



$$-O-\overset{O^{-}\,Na^{+}}{\underset{O}{P}}-O-\overset{O}{\underset{Na^{+}\,O^{-}}{P}}-O-$$

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).



Chain-like skeleton in the structure of a $ZBLAN_{6.6}$ glass (57.0 ZrF_4-28.1 BaF_2-3.3 LaF_3-5.0 AlF_3-6.6 NaF, in mol%).

(Adapted from: M.C. Goncalves and R.M. Almeida, Mat. Res. Bull. 31 (1996) 573)