Lecture 9

Chemical/Electronic Structure of Glass

Syllabus Topic 6. Electronic spectroscopy studies of glass structure

Examples of Chemical/Electronic Structure of Glass

Implications for properties

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Examples of applications of XPS

1. Processing

   Float glass

   Gel to glass transformation

2. Performance

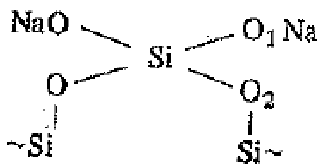
   Corrosion

3. Properties

   Electrical conductivity / dielectric constant of sodium aluminosilicate

Supplemental info on Blackboard: XPS of glass by C.G. Pantano

Relation between core level BE, atomic charge, and bond ionicity



Pauling: Ionicity of a bond between A and B:

$$I_{AB} = 1 - \exp\left[-0.25(\chi_A - \chi_B)^2\right],$$

Net charge on atom A, q_A, depends on its formal charge, Q_A and all the bonds that it forms i.e.

$$q_A = Q_A + \sum I_{AB},$$

In various alkali and alkaline earth silicates (Clarke and Rizkalla, Chem Phys. Lett. (1976)):
Si 2s (or O 1s) BE ∝ calculated charge from bonds that O forms with other metals.

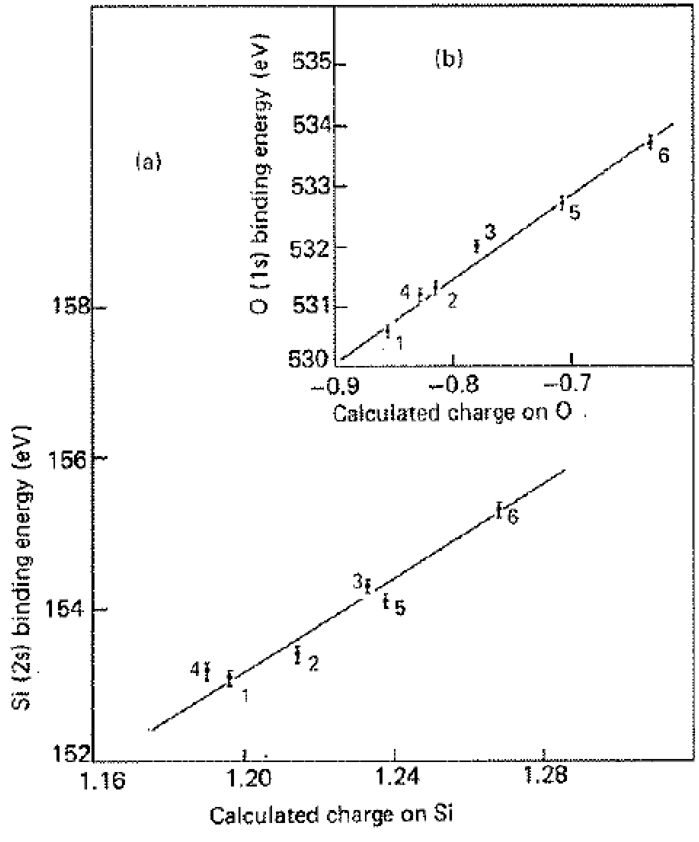


Fig. 1. Binding energy–charge correlation for (a) the silicon atom, (b) the oxygen atom.

XPS BE gives experimental ionicity of a bond.

Brow and Pantano, J. Am. Ceram. Soc. (1986)

Relative hydrophobicity of two sides of float glass

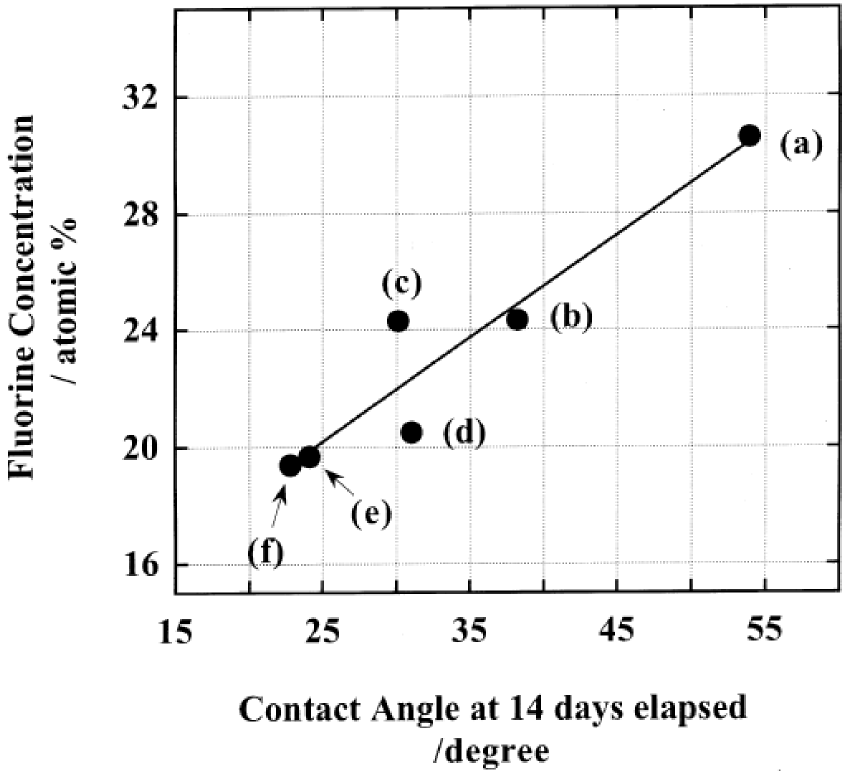


Fig. 3. The relationship between the fluorine concentration obtained from XPS measurements and the contact angle of water droplets at 14 days elapsed; (a) the bottom face of soda-lime float glass, (b) vitreous silica glass, (c) the top (b) face of soda-lime float glass, (d) boroaluminosilicate glass – type A, (e) boroaluminosilicate glass – type B and (f) boroaluminosilicate glass – type C.

F is used as a chemical label for surface OH.

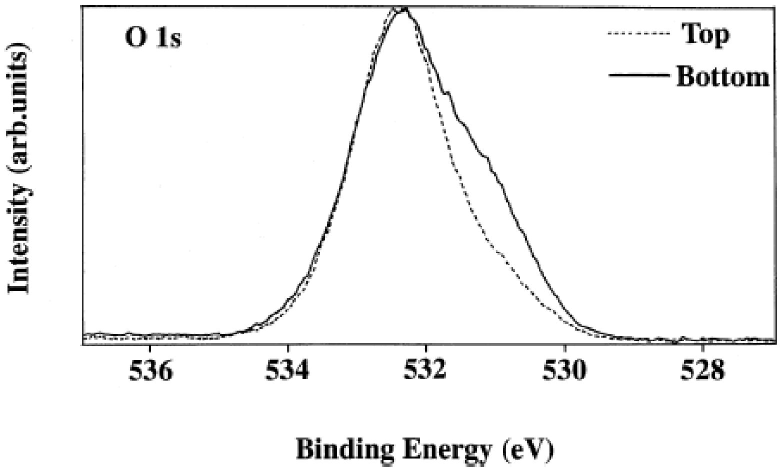


Fig. 5. High resolution O 1s XPS spectra for the top and bottom faces of soda-lime float glass.

The formation of SnOH group at the bottom surface enhances surface OH conc. and increases hydrophobicity.

Takeda, JNCS 249 (1999) 41-46

Are glasses prepared by the melt-quench and sol-gel processes the same?

Hypothesis: Sol-gel glass becomes identical to melt-quench glass upon heating to Tg.

$Si(OC_2H_5)_4 + H_2O \rightarrow \equiv Si\text{-}OH + C_2H_5OH$ (1)

$Si(OC_2H_5)_4 + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + C_2H_5OH$ (2)

$\equiv Si\text{-}OH + HO\text{-}Si\equiv \rightarrow \equiv Si\text{-}O\text{-}Si\equiv + H_2O$ (3)

$CH_3COOLi + H_2O \rightarrow Li^+ + OH^- + CH_3COOH$ (4)

Once the polycondensation reaction is complete, a higher temperature heat treatment of the gel obviously promotes depolymerization reaction by breaking up the $\equiv Si\text{-}O\text{-}Si\equiv$ chains:

$\equiv Si\text{-}O\text{-}Si\equiv + Li^+ + OH^- \rightarrow \equiv Si\text{-}O^- - Li^+ + \equiv Si\text{-}OH$ (5)

O-1s spectra for xLi_2O-(1-x)SiO_2 system.

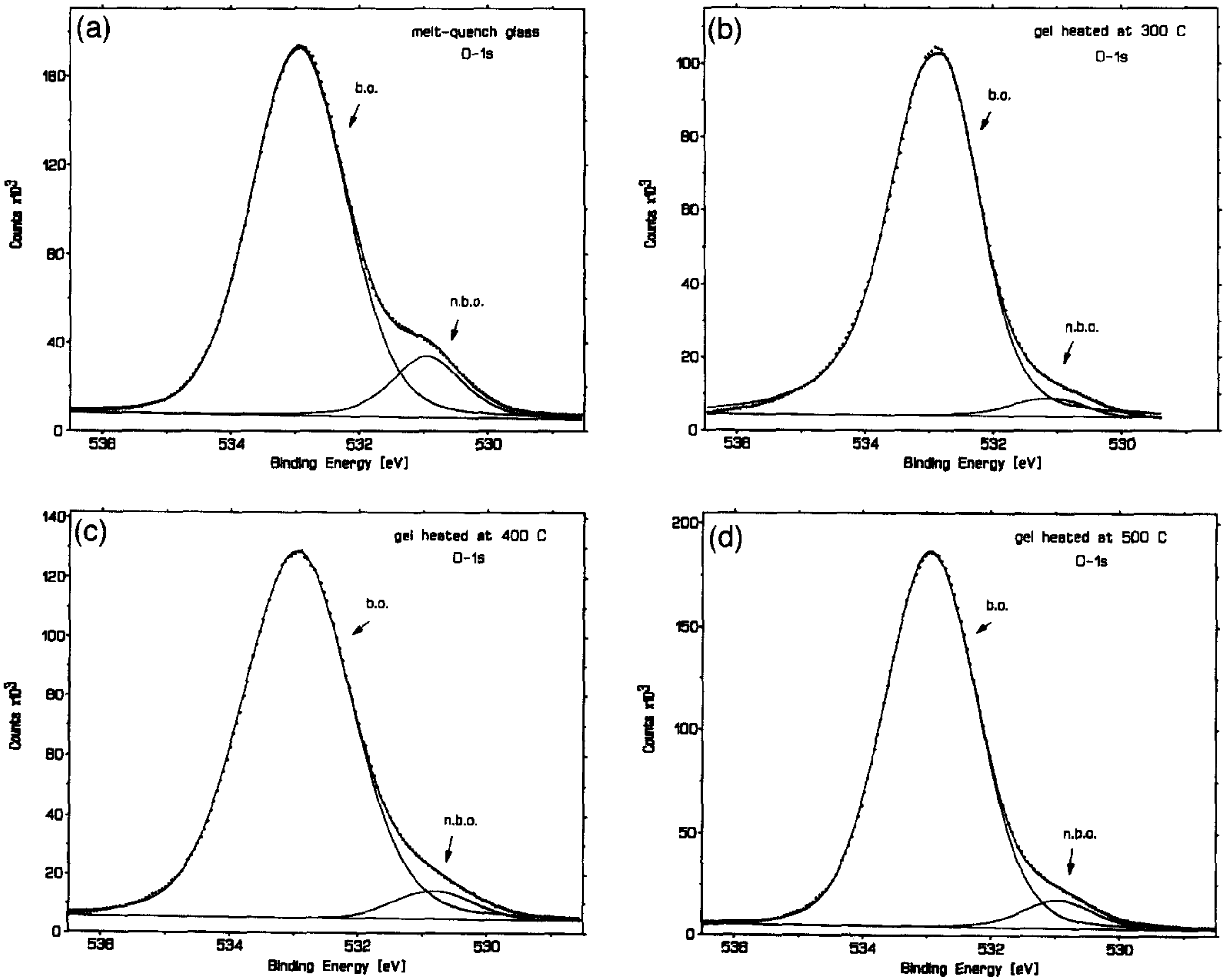


Fig. 2. Deconvoluted spectrum of O 1s for 15Li_2O–85SiO_2 system: (a) melt-quench glass; (b) gel heated to 300°C; (c) gel heated to 400°C; (d) gel heated to 500°C.

O-1s spectra for the $x\mathrm{Li_2O}$-$(1-x)\mathrm{SiO_2}$ system

As T ↑, the structure of gels → that of the melt-quench glass but does not become identical even on heating above *T*g. Phase separation occurs in gel much below *T*g. It occurs more readily in sintered gels than in the corresponding melt-quench glass.

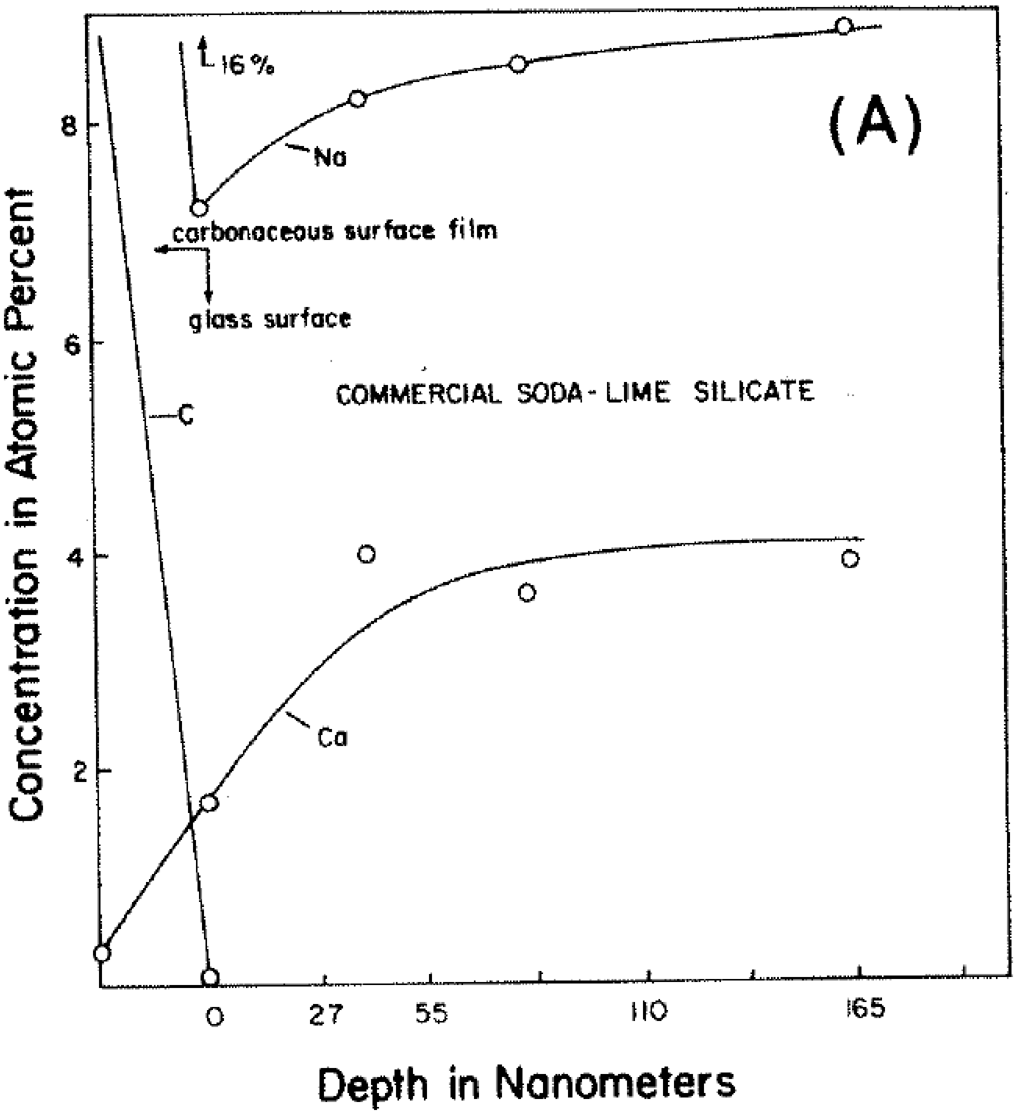
Theoretical value of n.b.o. mole fraction for x = 15% and 20% glasses is 16% and 22% respectively.

Specimen	Binding energy (eV)	FWHM (eV)	Area under the curve (%)
x=15% melt-quench glass	532.9(4) 530.9(4)	1.7(4) 1.2(9)	88.4 11.7
x=15% gel at 300^0 C	532.8 531.1	1.5 1.4	93.1 6.9*
x=15% gel at 400^0 C	532.9 530.8	1.9 1.5	95.1 5.2
x=15% gel at 500^0 C	532.9 530.9	1.7 1.3	94.4 5.8
x=20% melt-quench glass	533.0(2) 531.1(6)	1.6(7) 1.5(0)	81.4 18.9
x=20% gel at 300^0 C	532.9 531.1	1.7 1.3	93.0 7.4
x=20% gel at 400^0 C	532.2 530.2	1.9 1.3	93.2 7.5
x=20% gel at 500^0 C	532.9 530.8	1.8 1.4	89.5 10.9

What could be the basis of these conclusions?

Fraction of NBOs, and broad, asymmetric Li (Na) 1s XPS peak, observed in samples sintered at increasing temperatures.

Weathering of glass



Pantano, Bull Am Ceram Soc.

Physical properties of $x\text{Na}_2\text{O}$-$y\text{Al(vs. B)}_2\text{O}_3$-$(1-x-y)\text{SiO}_2$

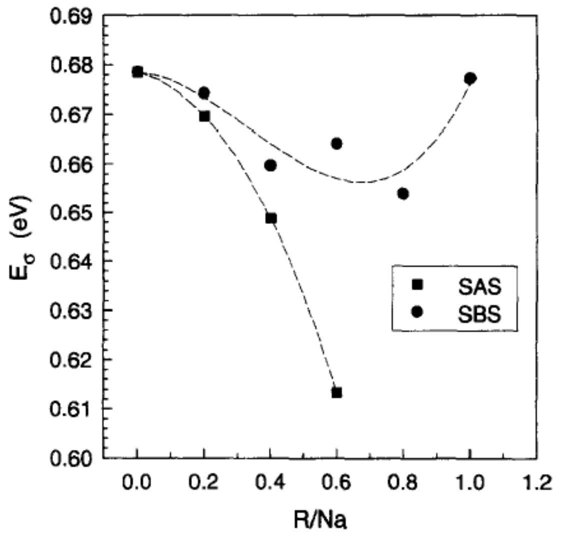


Fig. 4. Composition dependence of activation energy of ionic conduction in SAS and SBS glasses where R is Al or B. The datapoints are connected by lines using a third-order polynomial fit only to emphasize the trend.

Activation energy of ionic conductivity.

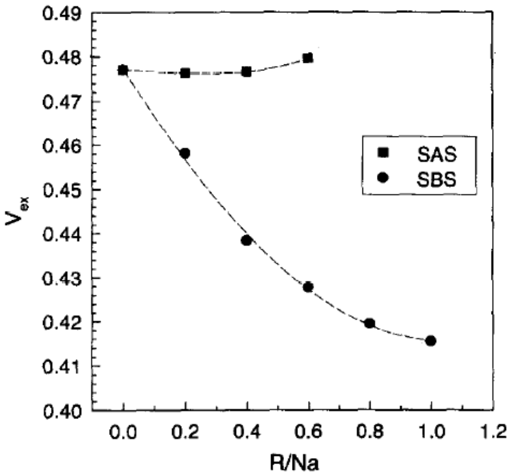


Fig. 5. Composition dependence of the fraction of excess volume in SAS and SBS glasses where R is Al or B. The datapoints are connected by lines using a third-order polynomial fit only to emphasize the trend

Excess volume calculated from density.

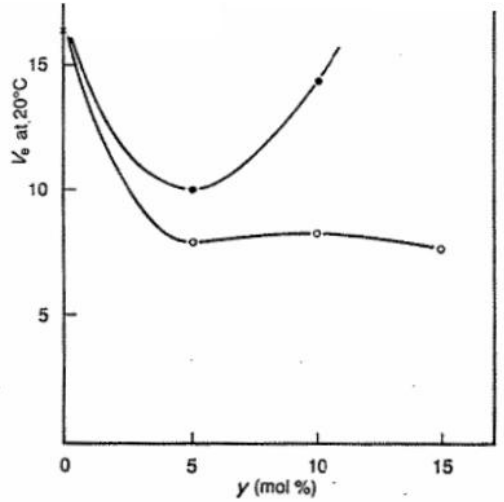
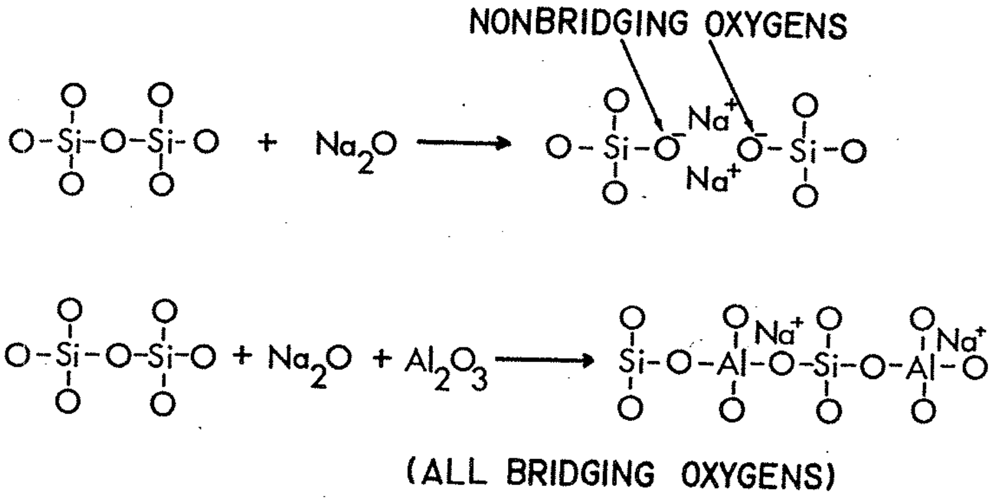


Figure 4 The dissolution rate v_e at 20°C for glasses in the systems $(0.30-y)\text{Na}_2\text{O}\cdot y\text{M}_x\text{O}_y\cdot 0.70\text{SiO}_2$ with *M* (●) Al, (○) B.

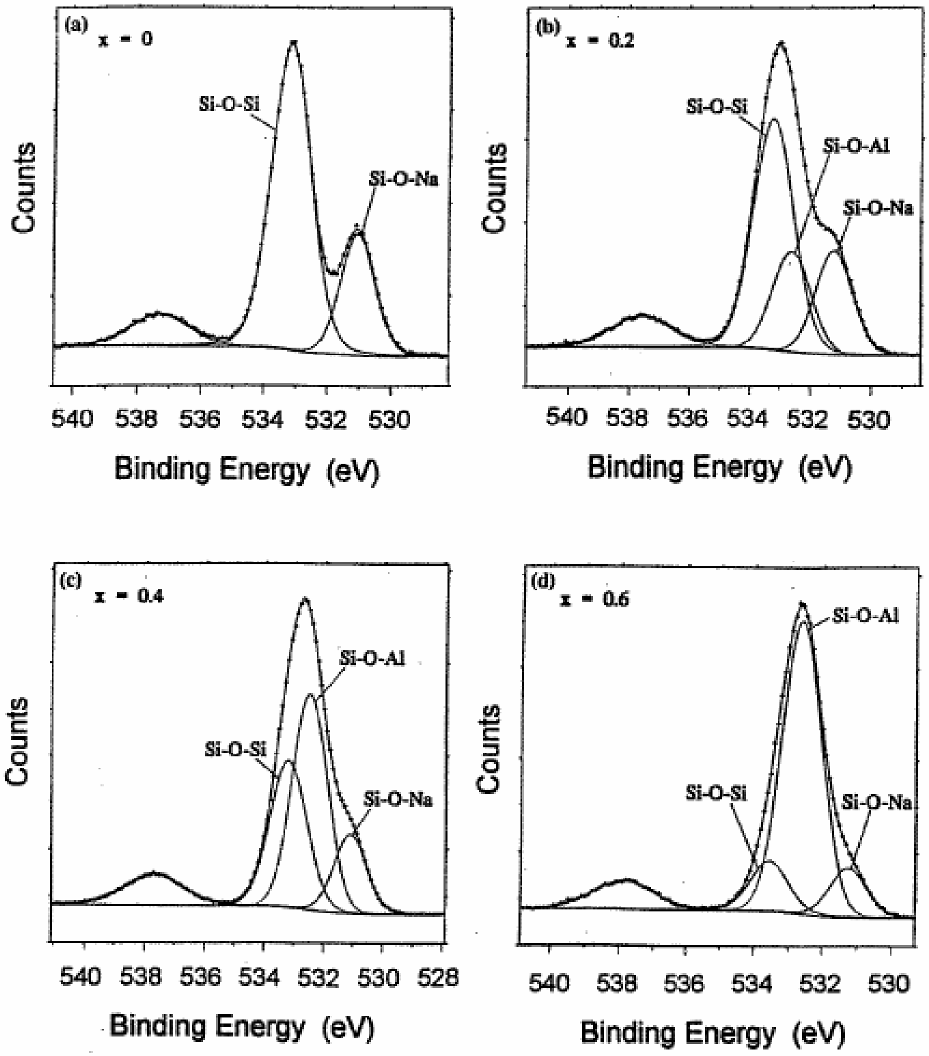
Dissolution rate at RT (different glass series).

Structure of $xNa_2O\text{-}yAl(\text{or }B)_2O_3\text{-}(1\text{-}x\text{-}y)SiO_2$



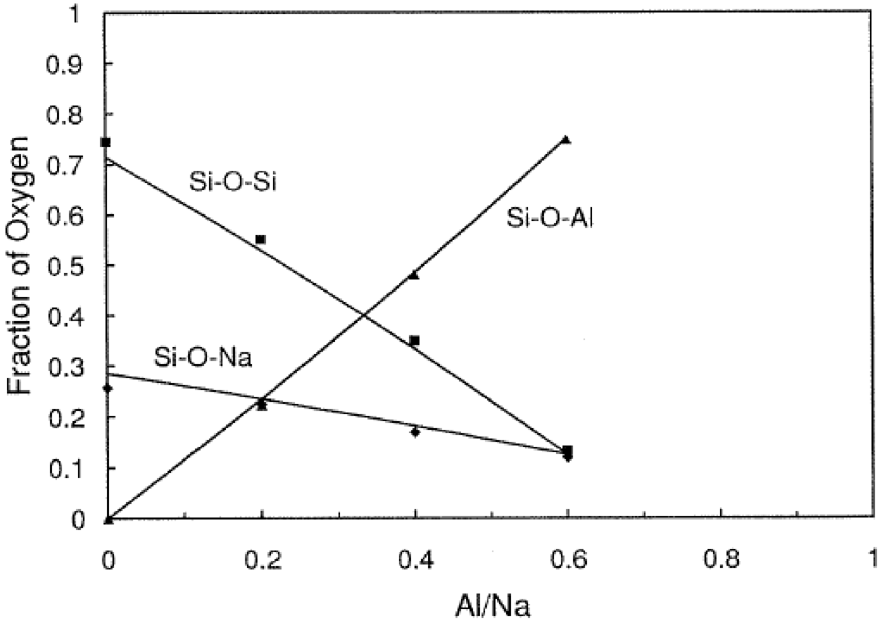
Spierings, J. Mater. Sci. (1991)

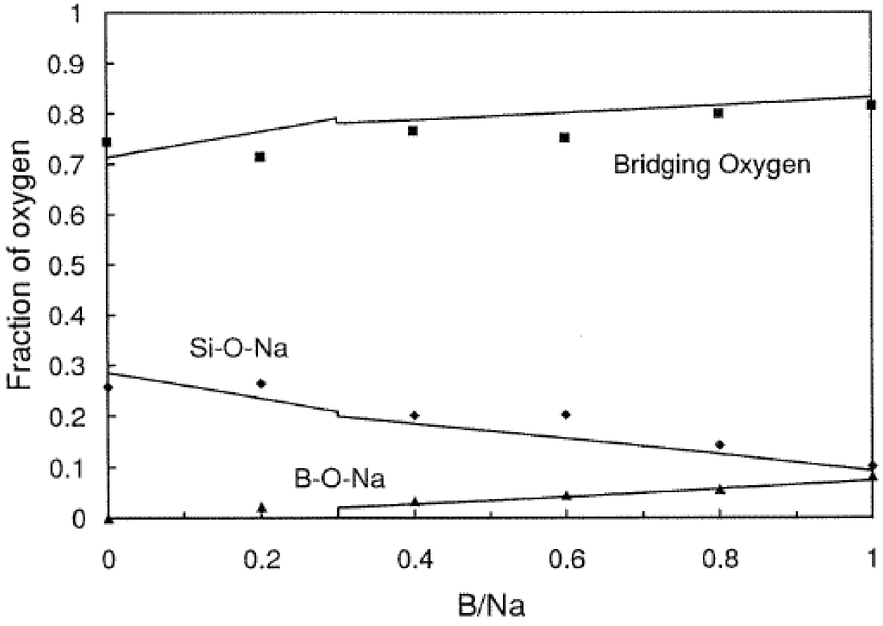
O 1s XPS $Na_2O\ x Al(\text{or } B)_2O_3(3\text{-}2x)SiO_2$



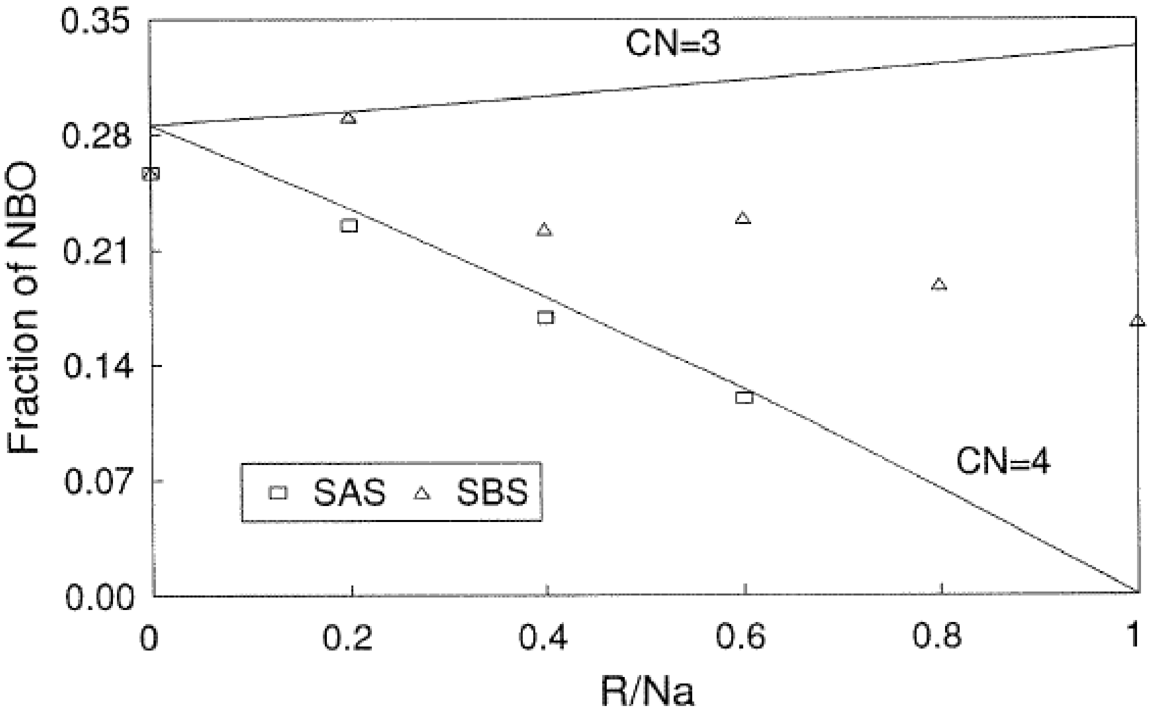
Ref: **H. Jain and C.H. Hsieh, in:** ***Diffusion in Amorphous Materials*****, ed. H. Jain and D. Gupta (TMS, Warrendale, PA, 1994) 63.**

O 1s XPS $Na_2O\ x Al(\text{or } B)_2O_3(3-2x)SiO_2$

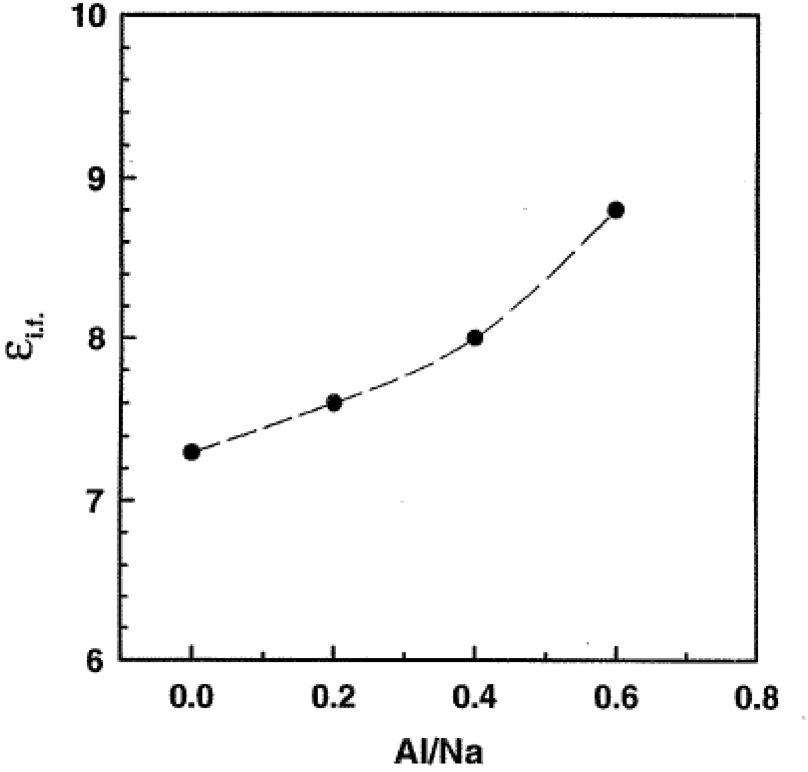




O 1s XPS_Na_2O xAl(or B)$_2O_3$(3-2x)SiO_2



Intermediate frequency dielectric constant of Na_2O xAl(or B)$_2O_3$(3-2x)SiO_2



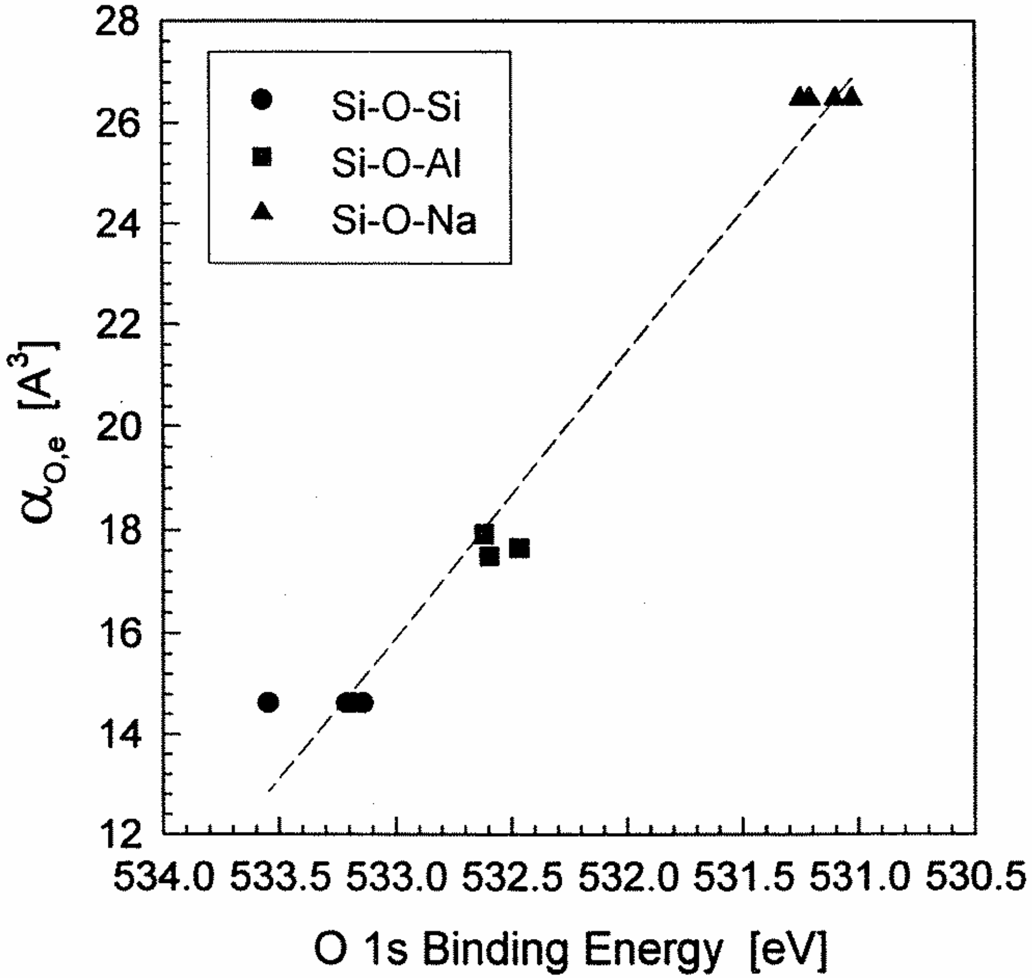
Dielectric constant below the optical frequencies depends on

(a) Electronic polarization
(b) Ionic polarization

Polarization = $\Sigma\ \alpha_e N_e + \Sigma\ \alpha_i N_i$

α is polarizability and N is #/vol of the atomic/molecular units.

Correlation between e-density around O and its electronic polarizability



α_e is calculated from refractive index

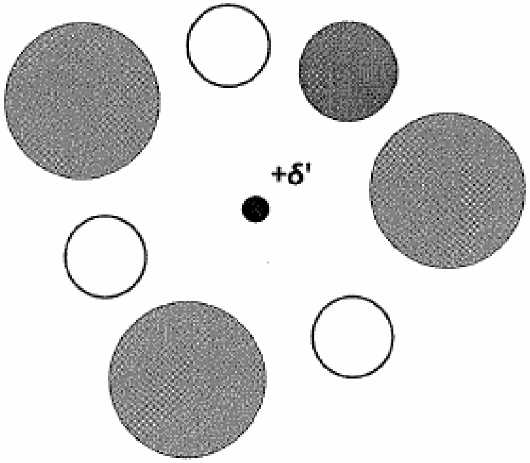
Ionic polarization

Oscillator model

$$\alpha^i = \frac{z^2 e^2}{(2\pi \nu_o)^2 m}$$

ze : charge on an atom
ν_o : lattice vibration frequency
m : reduced mass

$$\boxed{\alpha^i \propto z^2}$$

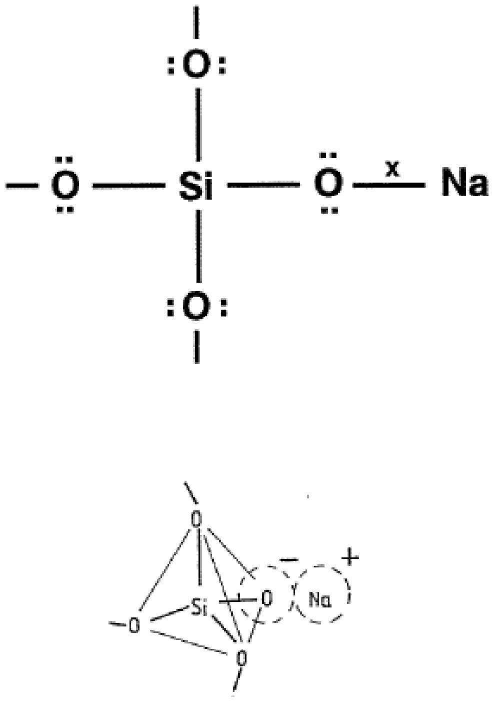


α^i_{Na}

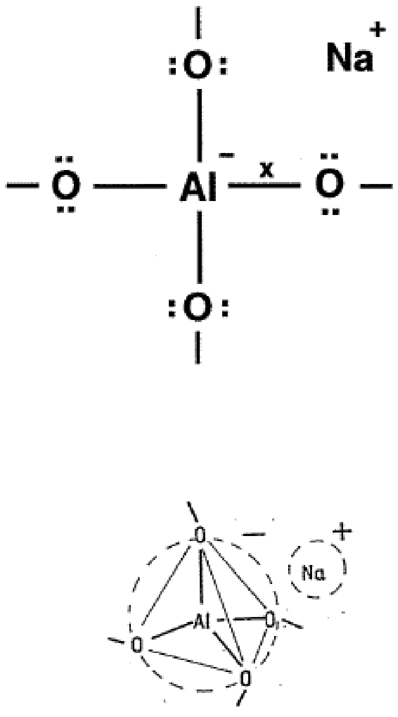
Ionic polarization in SAS glass

Na $3s^1$ Electron Structure

Na + NBO

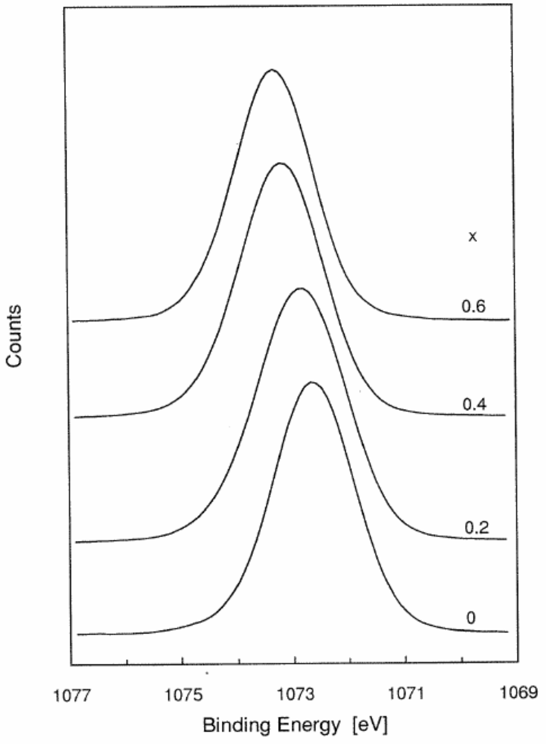


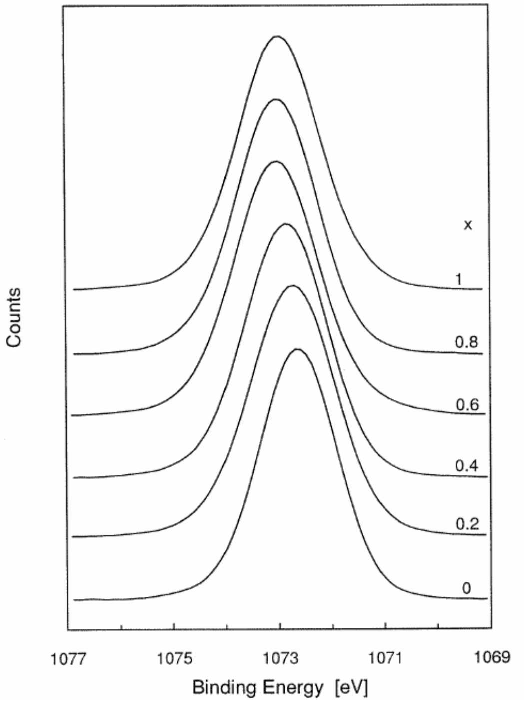
Na + $[AlO_4]^-$

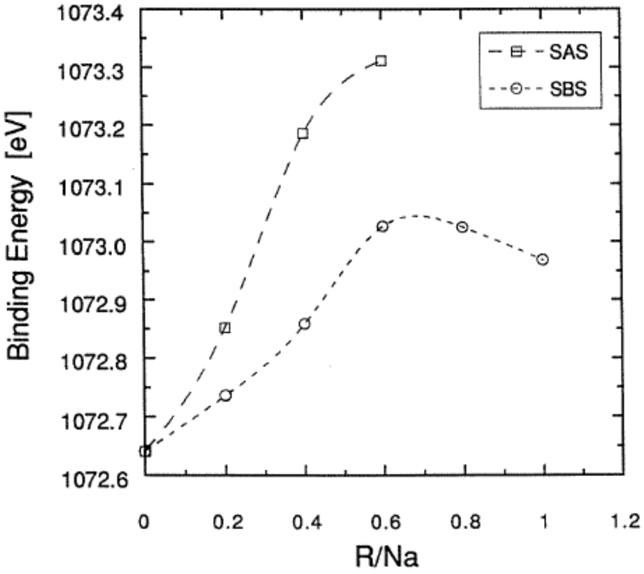


Na 1s in SAS and SBS glass series

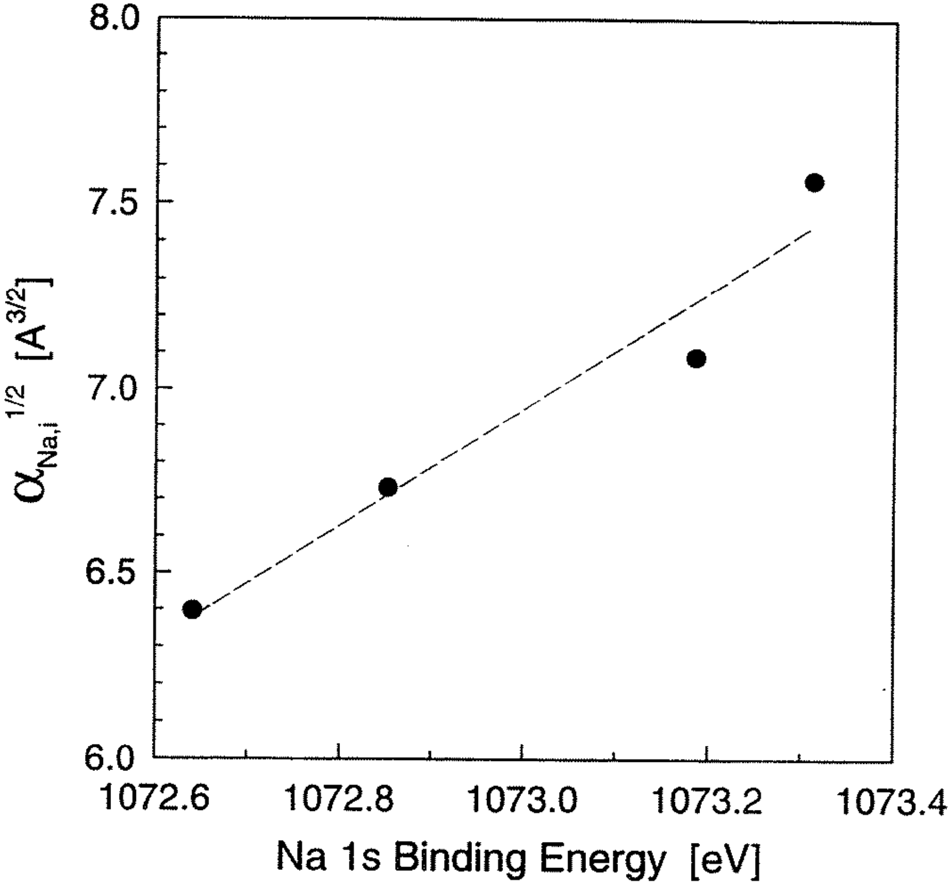
$Na_2O\ x\mathrm{Al(or\ B)}_2O_3(3-2x)SiO_2$







Correlation between Na ionicity and its ion polarizability



Short quiz

1. In angle resolved XPS, with increasing angle between the sample normal and detector, the probed depth (a) increases, (b) decreases, (c) does not change.

2. In relation to O 1s, the intensity of O 2s core level peak would be (a) higher, (b) lower, (c) the same.

3. Is the following statement correct? If not, explain what is wrong with it.

The spin orbit splitting of K 2s core level for a potassium silicate glass should be independent of glass composition.

4. Is the following statement correct? If not, explain what is wrong with it.

The charging of the sample surface would shift the various core levels by practically the same value.

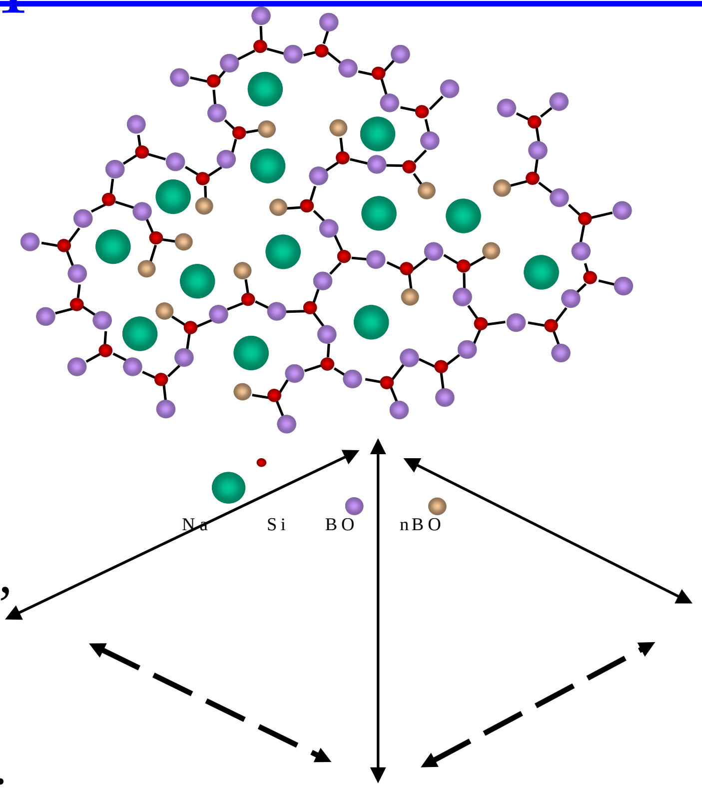
5. The ratio of O1s peak area for the non-bridging oxygen and bridging oxygen for a xNa_2O $(1-x)SiO_2$ glass is 0.3. What is the value of x?

Different Aspects of the Static Structure

Physical structure

Physical arrangement of atoms with respect to each other ($R_{M\text{-}O}$, $\Delta\sigma_{M\text{-}O}^2$, CN, etc..)

- Short range order.
- Medium range structure.



Chemical structure

- Nature of bonding (covalency, ionicity, basicity, etc...) between different kinds of atoms.
- Charge distribution.

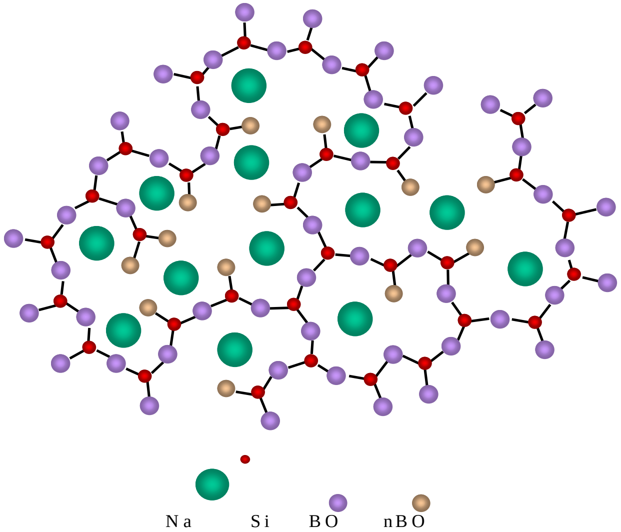
Vibrational structure

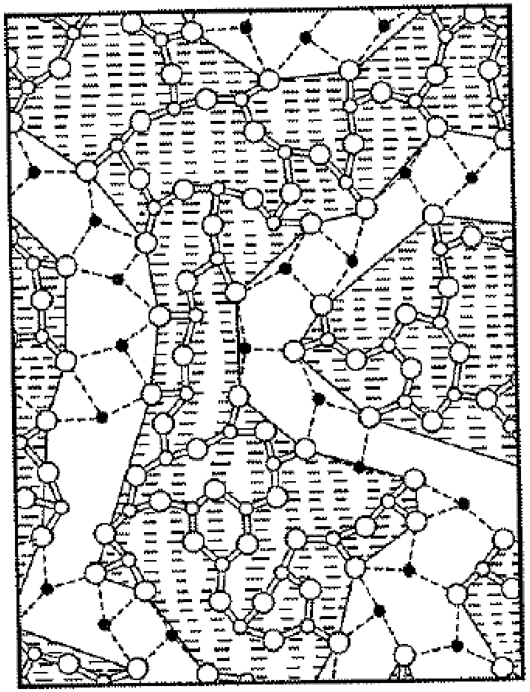
- Bond strength
- Local vibrations of the mobile atom.
- Vibrations of network structural units of small and medium size.

Elements of (physical) structure‘ - Shelby

1. Coordination of network cations/glass formers: Network building blocks, Short range order.
2. Bond Angle Distributions
3. Network Connectivity: Linkage of network forming polyhedra. Bridging vs Nonbridging Oxygens
4. Network Dimensionality: 3D: silica, 2D: B2O3, 1D: polymeric glasses (NaPO3?)
5. Intermediate Range Order: Linking of polyhedra to form larger, ordered molecular units- rings, chains- in an otherwise amorphous matrix.
6. Morphology: Phase separation? Network within a network?
7. Interstitial/Free Volume: Related to temperature dependence of properties: Thermal history effects, Gas diffusion sensitivity

Important schematics of glass strcuture





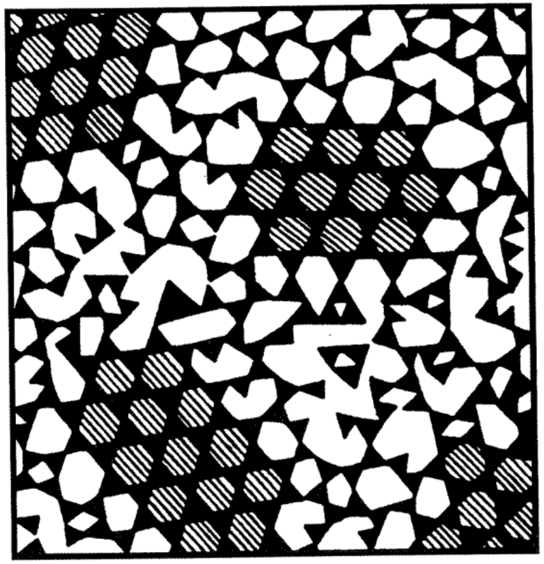
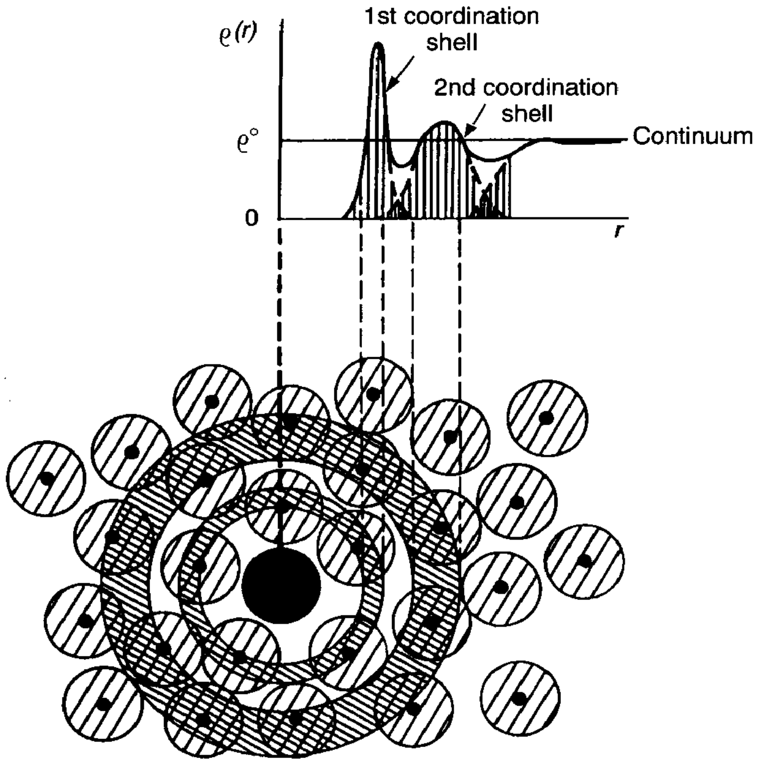


Figure 3-4. Schematic diagram of Lebedev's crystallite theory. Regions of local order (crystallites) are separated by regions of disorder.

Description of Non-crystalline Structure



15 Schematic illustration of the structural origin of the density function, $\rho(r)$, used to terize the structure of non-crystalline materials.

Average # density ρ_o= n/v

Pair distribution function, g(r) =ρ(r)/ ρ_o
ρ_o g(r)dr is probability of finding an atom between r and r+dr from origin.

Pair correlation function: h(r) = g(r) – 1
As r$\rightarrow\infty$, h(r)$\rightarrow$0 for glass i.e. no correlation or complete randomness.

Elliott, The Physics and Chemistry of Solids, Wiley, (1998)

Radial distribution function (RDF):

$J(r) = 4\pi r^2\rho(r) = 4\pi r^2\rho_o g(r)$

Area under the first peak in J(r) vs r plot gives the number of NN or the CN.

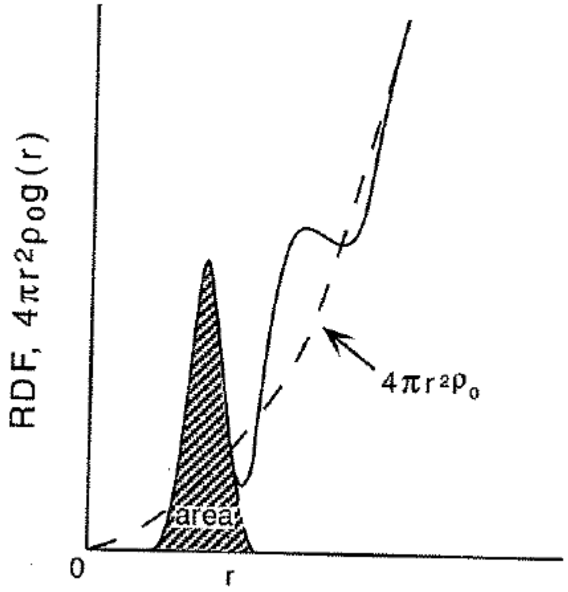


Figure 2-2b. Radial distribution function versus r. For uniform probability, the RDF is simply a parabola.

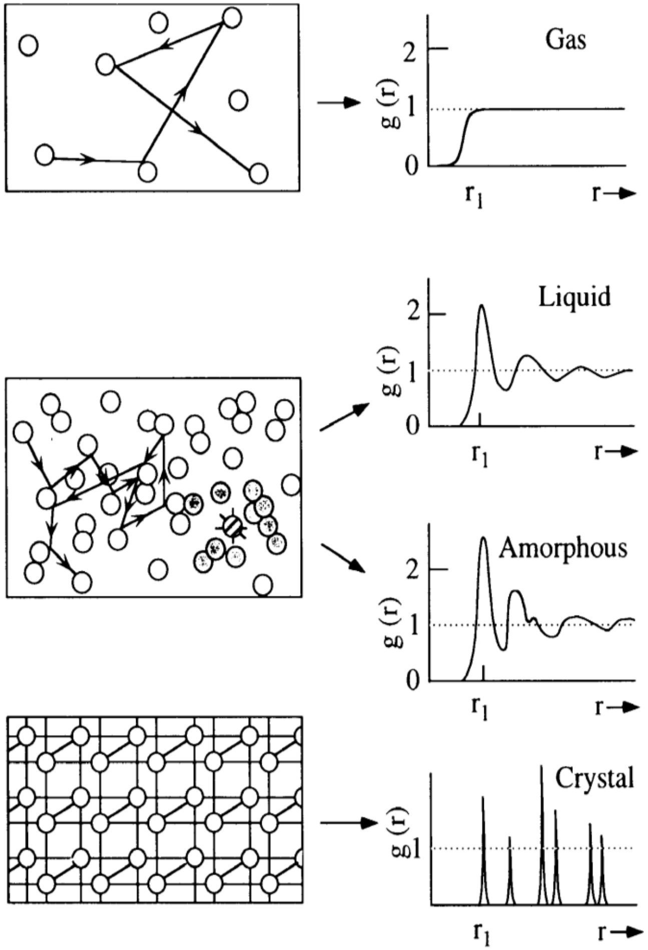


Figure 2-4. Schematic diagram of the atomic and pair distribution function for gas, liquid, amorphous, and crystal states. In gases, because of the kinetic energy, the atoms "penetrate" into each other slightly more deeper than in the condensed state. (Modified and redrawn from Y. Waseda, *Metal Phys. Seminar* **1**, 305 (1976).)

Varshneya: Fundamentals of Inorganic Glasses, 2006

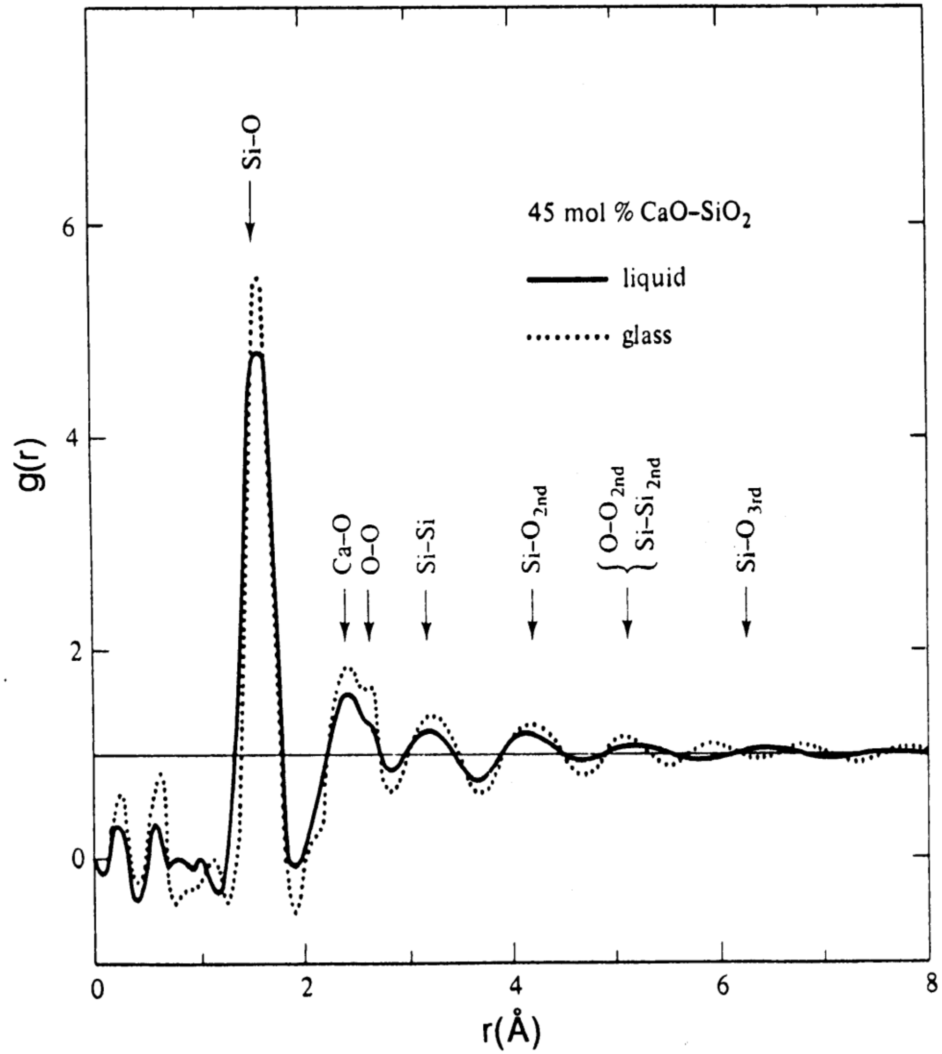


Figure 2-5. Comparison of $g(r)$ between the glassy and the liquid states for $45CaO{\cdot}55SiO_2$. (After Y. Waseda and J. M. Toguri, *MeT. Trans.* **8B**, 563 (1977).)