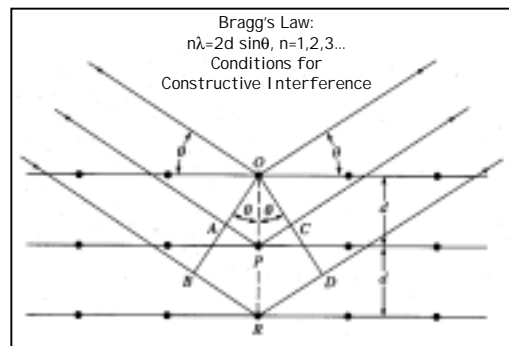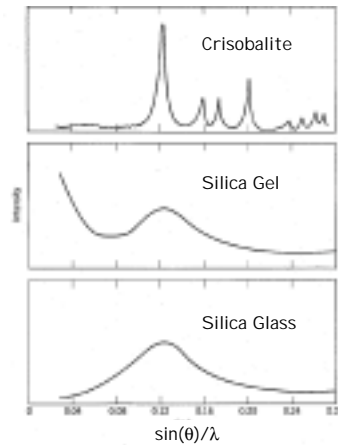## Structural Theories of Glass Formation

Zachariasen's Random Network Theory- 1932 (see Shelby pp. 7-10)

- Before Zachariasen, glass structures were considered to be comprised of nanocrystals- ~20Å size- estimated from broadening of diffraction patterns: 'breadth'~$0.9\lambda/(t \cos\theta)$, where λ is the x-ray wavelength, t is the particle size, θ the Bragg angle.

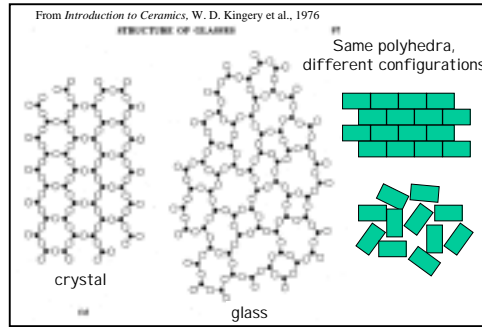- Problems: glass densities are too small (~10%) and no SAXS in diffraction pattern

Bragg's Law describes the conditions for constructive interference, and so the angle of incident x-rays that will produce intense diffraction peaks. Other diffraction angles will lead to destructive interference. The angle is related to the wavelength of the incident x-rays (λ) and the lattice spacings.

Zachariasen (crystallographer) noted similar mechanical properties (elastic modulus, etc.) between glasses and crystals and so expected similar structural energies $\rightarrow$ similar underlying atomistic building blocks (cation polyhedra).
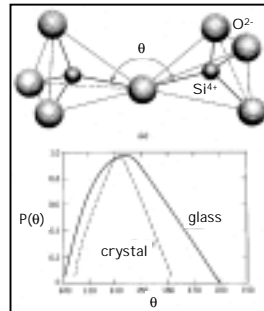
However, glasses have greater structural energies/amorphous structures
- Glasses lack the periodic (long range) order of a crystal
  - Infinite unit cell (no repeating large scale structures)
  - 3D network lacking symmetry and periodicity
  - ISOTROPIC: same average packing and properties in all directions
- Crystals in different directions(see above):
  - different atom packing and so different properties

Glasses possess a *Continuous Random Network*

Glasses and crystals have the same building blocks (cation polyhedra) arranged in different patterns; e.g., glasses have broader distributions of bond angles:

Zachariasen recognized that crystal chemistry rules and patterns also apply to glasses. Certain polyhedra are more likely to form the disordered networks particular to a glass:

"….the substance can form extended 3D networks lacking periodicity with an energy content comparable with that of the corresponding crystal network."

Oxides like SiO_2, B_2O_3, GeO_2, P_2O_5 form glasses, whereas oxides like MgO, Al_2O_3, Na_2O, CaO do not. *Why?*

Zachariasen's Rules for Glass Formation: (empirical observations for oxides)

1. No oxygen atom may be linked to more than <u>two cations</u>

2. The cation coordination number is small: 3 or 4.

3. Oxygen polyhedra share corners, not edges or faces.

4. For 3D networks, at least three corners must be shared

In general, all four rules should be satisfied for glass formation to occur.

Low coordination numbers, corner-sharing rules imply that glass formation is more likely with open, low density polyhedral structures.

1. Consider Silica:
    - covalent Si-O bond: sp^3 hybrid
      - tetrahedral bonding
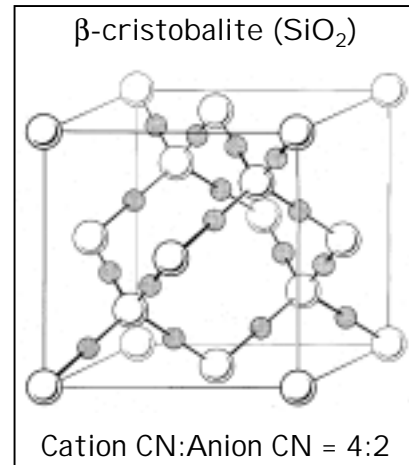 - Pauling's packing rule:

$$\frac{r(Si^{4+})}{r(O^{2-})} = \frac{0.40}{1.40} \approx 0.29 \quad \textit{prefers tetrahedral bonding}$$

  - satisfies Zachariasen's rule #2.

$$\frac{charge(Si^{4+})}{CN(Si^{4+})} = \frac{4}{4} = \frac{charge(O^{2-})}{CN(O^{2-})} = \frac{2}{2} \quad CN(O^{2-}) \textit{ is 2.}$$

  - satisfies Zachariasen's rule #1.

Crystal structure: sharing four corners:
   All Rules are Satisfied: SiO_2 forms a glass.

β-cristobalite (SiO_2)

Cation CN:Anion CN = 4:2

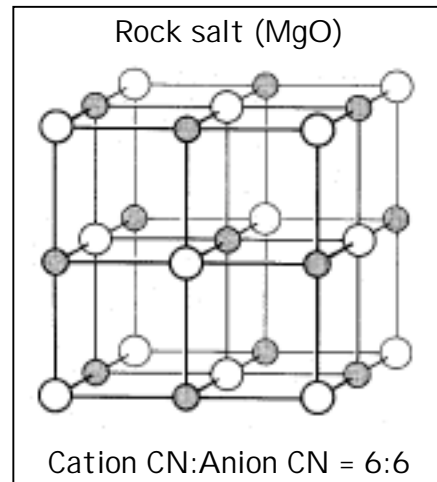2. Consider Magnesia (MgO):
  - ionic Mg-O bond
    - Pauling's packing rule:

$$\frac{r(Mg^{2+})}{r(O^{2-})} = \frac{0.72}{1.40} \approx 0.51 \quad \textit{prefers octahedral bonding}$$

  - violates Zachariasen's rule #2.

$$\frac{charge(Mg^{2+})}{CN(Mg^{2+})} = \frac{2}{6} = \frac{charge(O^{2-})}{CN(O^{2-})} = \frac{2}{6} \quad CN(O^{2-}) \textit{ is 6.}$$

  - violates Zachariasen's rule #1.

Crystal structure: edge-sharing polyhedra;
   Rules are Not Satisfied: MgO does not form a glass.

Rock salt (MgO)

Cation CN:Anion CN = 6:6

In general: *oxides with small cations (and so- small CN's) form glasses;
    - partial covalent bonding → hybridization, low CN geometries
*oxides with large, low valence cations (MgO, CaO,… Li_2O, Na_2O,…) do not form glasses.
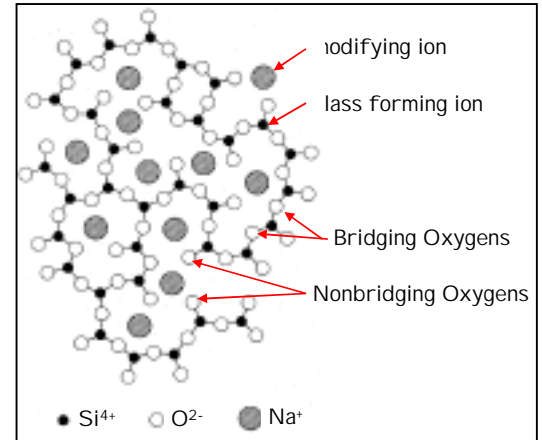   - dominated by ionic bonding; higher CN's

So- what happens when a 'non-glass former' is added to a 'glass former'?

Retain the continuous random network (CRN) of the glass former, but that network has been *modified* the addition of the second oxide.

- These ionic compounds are called *Glass Modifiers*.

Bridging Oxygens link glass forming tetrahedra.

Nonbridging Oxygens form the ionic bonds with the modifiers

3. Consider Alumina (Al_2O_3):
   - Pauling's packing rule:

$$\frac{r(Al^{3+})}{r(O^{2-})} = \frac{0.53}{1.40} \approx 0.38 \quad octahedral / tetrahedral\ boundary$$

   - octahedral CN preferred in Al_2O_3.

$$\frac{charge(Al^{3+})}{CN(Al^{3+})} = \frac{3}{6} = \frac{charge(O^{2-})}{CN(O^{2-})} = \frac{2}{4} \quad CN(O^{2-})\ is\ 4.$$

   - violates Zachariasen's rule #1.

   Al_2O_3 does not form a glass.

However, in aluminosilicate crystals:
   Al-CN = 4
   O-CN = 2,
Zachariasen's rules are obeyed $\rightarrow$ aluminosilicate glasses
   Important geological and technological applications

Such oxides are called *Intermediates* or *Conditional Glass Formers*
- do not form glasses by themselves, but act like glass formers when combined with others (aluminosilicate, aluminoborate, aluminophosphate glasses).

Importance of Zachariasen?
- First to apply crystal chemical principles to the study of glass structure and properties;.
    - First to note the similarities in SRO between glasses and crystals.
- Established the *Continuous Random Network* paradigm for glass structure;
- First to classify the structural roles for component oxides;
    - Glass formers, modifiers, intermediates

Since then others have applied additional crystal chemical principles for defining glass structure and formation roles:

1. *Dietzel* (1942) examined direct Coulombic interactions:

$$attractive\ force = \frac{(z_c e)(z_a e)}{(r_c + r_a)^2}$$

Let $a = (r_c + r_a)$ and (for oxides) $z_a = -2$; then Dietzel categorized cations using:

$$Field\ Strength = z_c/a^2$$

High F. S. cations $\rightarrow$ high cation-oxygen bond energy:

	z_c/a^2
Glass Formers	>1.3
Glass modifiers	<0.4
Intermediates	$0.4 \leq FS \leq 1.3$

2. *Sun* (1947) considered a single bond strength approach:

Dissociation energy for a molecule, E_d: $A_x O_y \rightarrow xA + yO$

$$single\ bond \sim E_d/CN\ (kcal)$$

Dissociation energy is related to thermodynamic lattice energy:
- Estimated from Coulombic attraction: $\sim(e^2 Z^2/r_0)A$
    - A is Madelung constant, accounts for longer range Coulombic interactions
- Can be determined from compressibility measurements;
    - Bulk modulus $\sim -v\ d^2U/dV^2$
- Can be determined from heat capacity measurements:
    - $C_v \sim (dU/dT)_v$ (at low temps); etc.

Sun noted:
- High S.B. strength oxides (>80 kcal/bond) $\rightarrow$ glass formers
- Low S. B. strength oxides (<60 kcal/bond) $\rightarrow$ glass modifiers
- Intermediate S.B.S. oxides (60-80 kcal/bond) $\rightarrow$ intermediates

How do the Sun criteria relate to melt crystallization?
  High bond strengths, difficult to break/reform into ordered lattice upon cooling
  High bond strengths, high viscosity, so good glass formers
  Low bond strengths, easy to break/reform into preferred crystal.

3. *Stanworth* (1971) noted similar patterns with electronegativity/ion size

> J. E. Stanworth, *J. Amer.*
> *Ceram. Soc.*, **54** (1971)

4. *Izumatani* Table summarizes various ion properties:

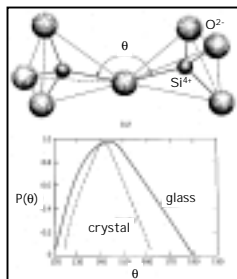From Izumatani, *Optical Glass*, AIP Trans. Series, NY 1986

Table 1.2. Glass forming substances and physical properties that act as measures.

	Ion	Ionic bonding of oxide (%)	Coordination number	$2z/a^2$	Electro-negativity	Single bond strength (kcal)
Glass forming oxides	P^{5+}	39	4	4.3	2.1	88 to 111
	B^{3+}	42	3	3.22	2.0	119
	Si^{4+}	50	4	3.14	1.8	106
	Ge^{4+}	55	4	2.65	1.8	108
Intermediate oxides	Al^{3+}	60	(6)	1.69	1.5	53 to 67
	Be^{2+}	60	4	1.51	1.5	63
Modifier oxides	Mg^{2+}	70	6	0.95	1.2	37
	Zn^{2+}	—	4	0.91	—	36
	Ca^{2+}	75	8	0.69	1.0	32
	Sr^{2+}	75	8	0.58	1.0	32
	Pb^{2+}	—	6	0.53	—	39
	Ba^{2+}	80	8	0.51	0.9	33
	Li^{+}	75	4	0.48	1.0	36
	Na^{+}	80	6	0.35	0.9	20
	K^{+}	83	9	0.27	0.8	13
	Cs^{+}	82	12	0.22	0.7	10

Note: all these *empirical* crystal chemical approaches describe which compounds are likely to form glasses; no predictions about how easily glass formation might be. We need to return to our *kinetic description* (nucleation and growth) for that information.

Structures of Glasses (Shelby Chapter 5)

Glasses have well-defined short range (nearest neighbor) bond arrangements;

- Precisely measured CN, bond lengths

- Fairly well determined bond angle distributions.
  - Breadth of this distribution that is responsible for the loss of long-range order.

Shelby defines the 'elements of structure'; what do we need to know to describe the atomic networks of glasses? Dependent upon length scale:

1. Coordination of network cations/glass formers
   - Network building blocks
   - Short range order
   - Determined by a variety of spectroscopic probes

2. Bond Angle Distributions
   - Experimentally difficult (diffraction)

3. Network Connectivity
   - How are neighboring glass forming polyhedra linked?
     - Bridging and Nonbridging Oxygens

4. Network Dimensionality
   - 3D: silica
   - 2D: B_2O_3
   - 1D: polymeric glasses ($NaPO_3$?)
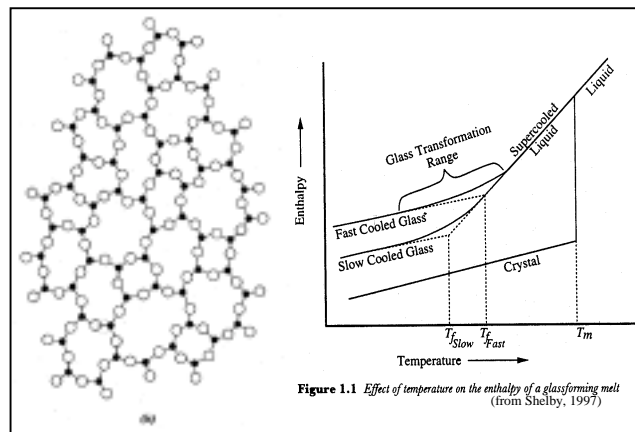
5. Intermediate Range Order
   - Linking network building blocks (polyhedra) to form larger, ordered molecular units- rings, chains- in an otherwise amorphous matrix.

6. Morphology
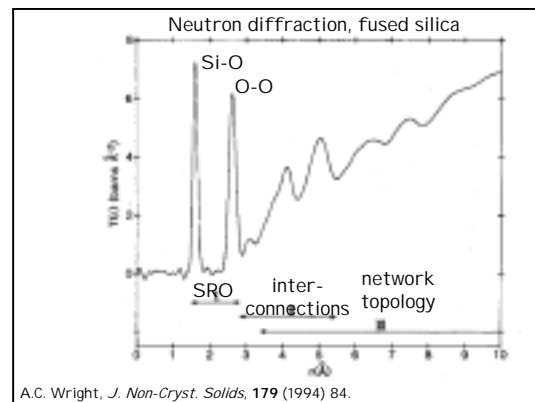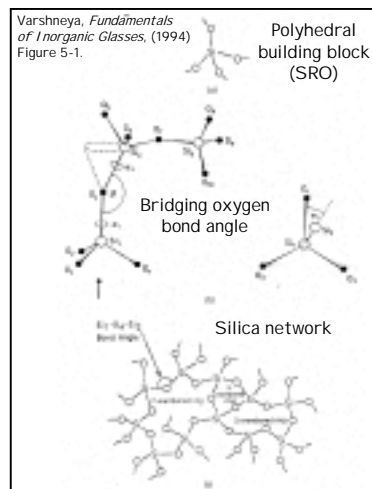   - Phase separation? Network within a network?

7. Interstitial/Free Volume
   - Related to temperature dependence of properties
   - Thermal history effects
   - Gas diffusion sensitivity

Figure 1.1 *Effect of temperature on the enthalpy of a glassforming melt*
(from Shelby, 1997)

I. Structural Models for Silica

- Vitreous silica: prototypical 'Zachariasen glass'.
  - High T_g (1200°C)
  - SiO_4 tetrahedra (Zachariasen rule #2)
  - Oxygens are coordinated to two silicons (Z. rule #1): All BRIDGING OXYGENS
    - 4:2 silica network
  - Corners are shared (rule 3) in three dimensions (rule 4)

- SiO_4 tetrahedra are very well defined (from x-ray, neutron diffraction)
  - Si-O distance: 1.62Å
  - O-O distance: 2.65 Å
    - Same as found in crystalline SiO_2
  - Si-O-Si bond angles: ~144±10⁰ (distribution responsible for lack of LRO)

Varshneya, *Fundamentals of Inorganic Glasses*, (1994) Figure 5-1.

Polyhedral building block (SRO)

Bridging oxygen bond angle

Silica network

Neutron diffraction, fused silica

Si-O
O-O

SRO   inter-connections   network topology

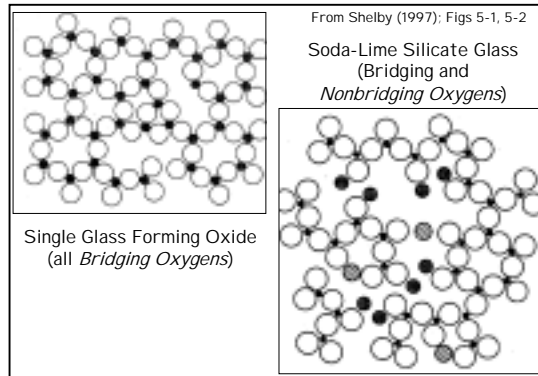A.C. Wright, *J. Non-Cryst. Solids*, **179** (1994) 84.

I.1 Binary Alkali Silicates
- Batched from silica and alkali carbonates or nitrates
  - Immiscibility ranges: 0-33 mole% Li_2O
    0-20 mole% Na_2O
- *Alkalis are Fluxes*
  - Decrease viscosity (orders of magnitude)
  - Decrease T_g
  - Increase density, refractive index, CTE, etc.
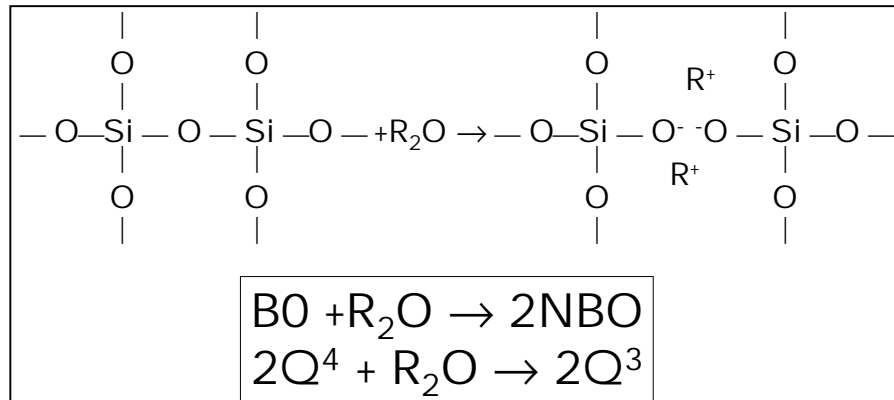 - Increase electrical conductivity

What accounts for these property changes?

Note: adding alkalis increases ion density, 'filling in' the holes in the network

From Shelby (1997); Figs 5-1, 5-2

Soda-Lime Silicate Glass
(Bridging and
Nonbridging Oxygens)

Single Glass Forming Oxide
(all *Bridging Oxygens*)

Alkalis are structural modifiers:
- Every alkali ion creates one new NBO;
- Every alkali oxide 'molecule' creates two NBO's

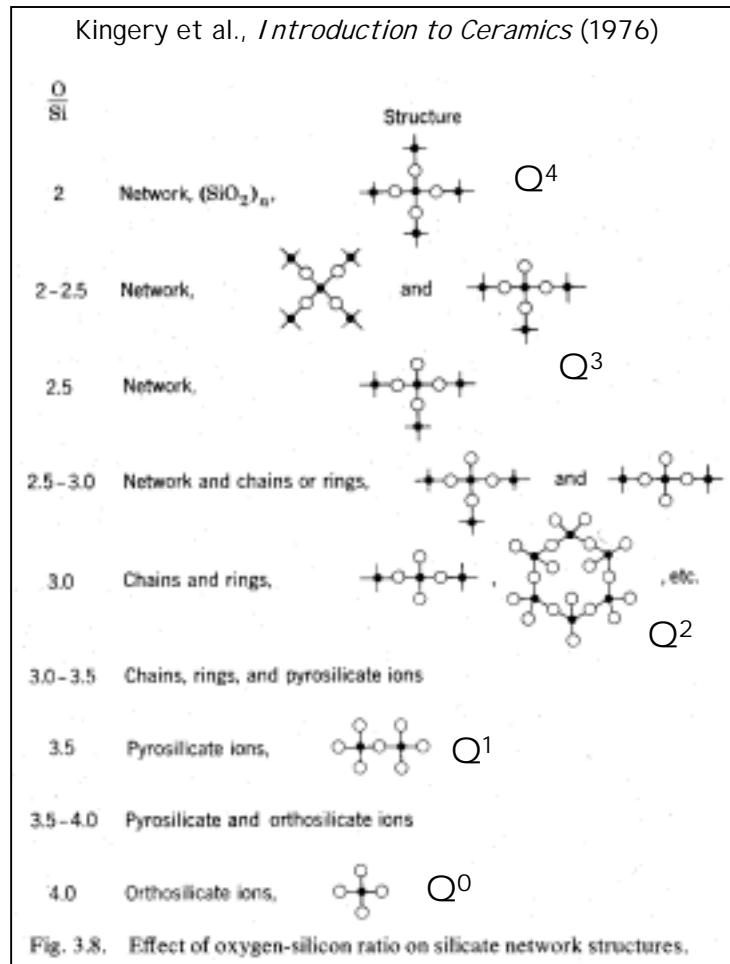$$BO + R_2O \rightarrow 2NBO$$
$$2Q^4 + R_2O \rightarrow 2Q^3$$

We can calculate the numbers of bridging and nonbridging oxygens and use those numbers to explain glass properties.

Definitions for 'Q^x' terminology:
- 'x' is the number of bridging oxygens on a tetrahedron (Shelby uses subscripts, the convention is superscript).

- The structure of silica consists of Q^4-tetrahedra (four bridging, no nonbridging oxygens).
- Modifying oxides create lower 'Q^x' structures by replacing bridging oxygens with nonbridging oxygens:
  - Q^3 tetrahedra: 3 bridging, 1 nonbridging oxygens per silicon
  - Q^2 tetrahedra: 2 bridging, 2 nonbridging oxygens per silicon
  - Q^1 tetrahedra: 1 bridging, 3 nonbridging oxygens per silicon
  - Q^0 tetrahedra: 0 bridging, 4 nonbridging oxygens per silicon

- Framework or tectosilicates, SiO_2: Si-tetrahedra with four bridging oxygens. Since each BO is shared by two silicons (1/2 BO/Si), stoichiometry is [O]/[Si]=2.0.

Nonbridging oxygens are not shared, so
- Orthosilicates (Nesosilicates): Q^0 structures
  - $(SiO_4)^{4-}$ anions, [O]/[Si]=4.0 stoichiometry.

- Pyrosilicates (Sorosilicates): Q^1 structures
  - $(Si_2O_7)^{6-}$ anions, [O]/[Si]=3.5 stoichiometry

- Metasilicates (Inosilicates, chains and Cyclosilicates, rings): Q^2 structures
  - $(SiO_3)^{2-}$ anions, [O]/[Si]=3.0 stoichiometry

- Phyllosilicates (Sheets): Q^3 structures
  - $(Si_2O_5)^{2-}$ anions, [O]/[Si]=2.5 stoichiometry

Kingery et al., *Introduction to Ceramics* (1976)

Fig. 3.8.   Effect of oxygen-silicon ratio on silicate network structures.
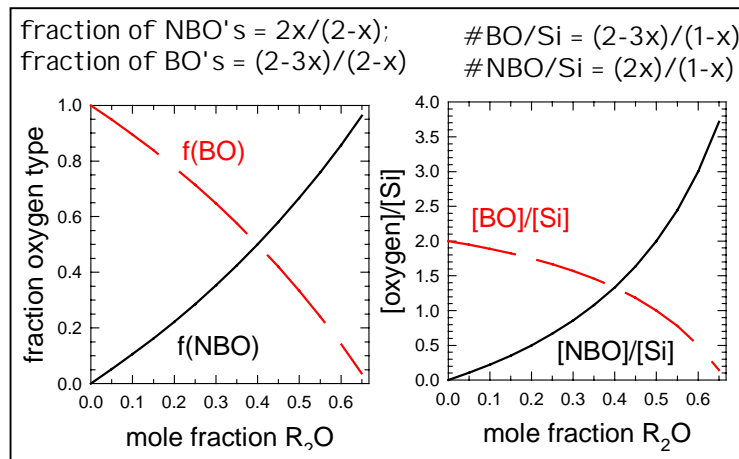
We can calculate the NBO fraction (or Q-distribution) from glass composition and so relate macroscopic properties to a quantitative measure of network connectivity.
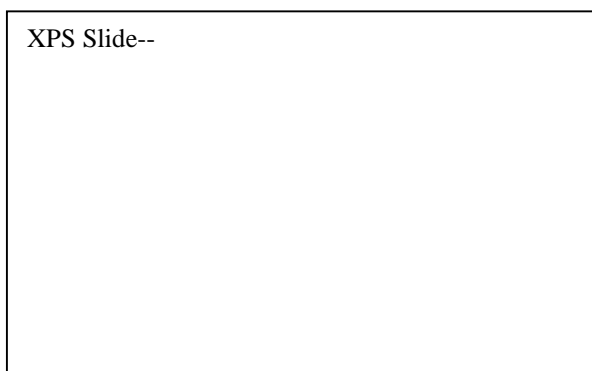- More modified structure, more NBO's, lower viscosity, lower T_g, etc.

Consider: xR$_2$O $(1-x)$SiO$_2$ glass; x = mole fraction R$_2$O.

- Total # of oxygens = $x + 2(1-x) = (2-x)$

- Since each R$_2$O creates 2 NBO's, Total # of NBO's is 2x

- Therefore,   the fraction of NBO's = $2x/(2-x)$;
               the fraction of BO's = $((2-x) - 2x)/(2-x) = (2-3x)/(2-x)$

- # of Si-tetrahedra = mole fraction SiO$_2$ = $(1-x)$;

- therefore,   #BO/Si = $(2-3x)/(1-x)$
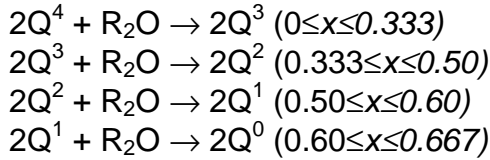   #NBO/Si = $(2x)/(1-x)$

We can characterize different oxygen sites using spectroscopic tools like XPS.

XPS Slide--

These relationships lead to the oxygen characteristics for various 'Q^{x}' silicons given by Shelby in Table 5-3.

The fractions of 'Q^{x}' tetrahedra can also be calculated from composition.

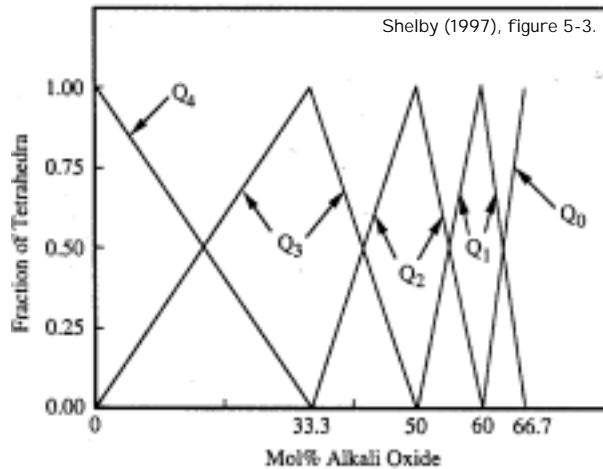Represent the 'modifier' effect using Q-terminology:

$2Q^4 + R_2O \rightarrow 2Q^3$ *(0≤x≤0.333)*
$2Q^3 + R_2O \rightarrow 2Q^2$ *(0.333≤x≤0.50)*
$2Q^2 + R_2O \rightarrow 2Q^1$ *(0.50≤x≤0.60)*
$2Q^1 + R_2O \rightarrow 2Q^0$ *(0.60≤x≤0.667)*

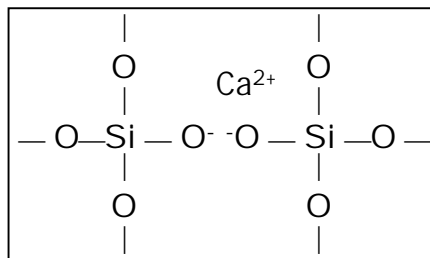Calculate Q-species distributions from composition?
  e.g., $f(Q^4)$ and $f(Q^3)$ when *0≤x≤0.333*
  - for xR_2O (1-x)SiO_2
    - $2x$ Q^3 tetrahedra created (one for each R^+ added)
    - total # of Si-tetrahedra is (1-x)
    - therefor, $f(Q^3) = 2x/(1-x)$ (=0 at x=0, =1 at x=0.333)

    - # of Q^4 tetrahedra=(total)-(# of Q^3) = (1-x) - 2x = (1-3x)
    - therefor, $f(Q^4) = (1-3x)/(1-x)$ (=1 at x=0; =0 at x=0.333)

Shelby gives other Q-distribution formulae in Table 5-4, and plots respective
distributions in figure 5-3. (See handout- word file 'Q-calculations'- for derivations
of various Q-distributions.

Shelby (1997), figure 5-3.

Alkaline earth oxides have similar 'depolymerizing' effect on network structure:

Note that one alkaline earth ion neutralizes two NBO's

- •   Same equations can be used to predict the effects of R'O additions on connectivity of silicate networks (use the same 'x', since one oxygen is added whether R'O or R_2O).

- • Effects on properties will depend on field strength (z/r_c^2) of modifying cation: how strong is that ionic NBO-R-NBO bridge between Q-sites?
  - •   Increasing r_c? Li^+-NBO stronger than Na^+-NBO stronger than K^+-NBO
    - • Cs_2O is the better flux…
  - •   Increasing valence? Mg^{2+}-NBO stronger than Li^+-NBO
    - •   Mg-glasses are more refractory…

Note: Network connectivity for $25Na_2O$ $75SiO_2$ and
                                  $15Na_2O$ $10CaO$ $75SiO_2$
       are the same. ([O]/[Si] = 2.33, so same NBO/BO, same Q-distributions)

       But, different properties (SLS more refractory, more durable).

Properties result from compositional compromises: Na_2O added to reduce melting temperatures, CaO helps prevent phase separation/crystallization and imparts better durability than binary sodium silicate.
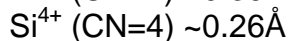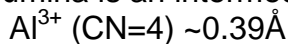
Note: Common representation of alkali incorporation is that they 'fill holes' in the glassforming framework or that they are single-bonded to NBO's (Shelby fig. 5-3)
- • Violates Pauling's rules for crystal chemistry
- • Alkali coordination polyhedra determined from radius ratios
- • Modern spectroscopy suggests that alkalis also have well-defined nearest neighbors (polyhedral arrangements).
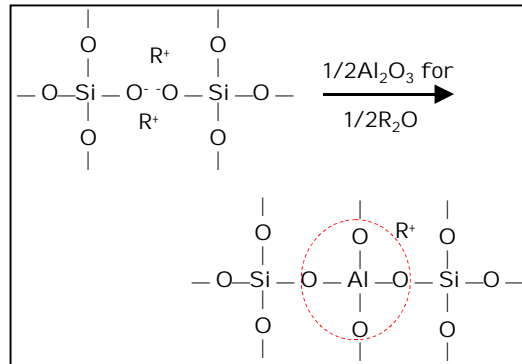
I.2 Aluminosilicate Glasses

- • Geological importance (earth's mantle is dominated by aluminosilicate, obsidian)
- • Technological importance- alkaline earth aluminosilicate fiber-glasses
                                  Alkali aluminosilicates for ion-exchange
                                  Li-aluminosilicates for glass-ceramics

Alumina is an intermediate oxide:
     Al^{3+} (CN=4) ~0.39Å
     Si^{4+} (CN=4) ~0.26Å
Close enough in size so that Al^{3+} replaces Si^{4+} in network sites. Note that each Si-O-Al bond is underbonded (1.75 VU= 1VU from $Si(IV)^{4+}$, 0.75 VU from $Al(IV)^{3+}$) and so the alkali (or alkaline earth) ions charge balance the new *network* site.

Al_2O_3 additions increase the connectivity of an alkali modified glass by replacing NBO's with cross-linking Al-O-Si bonds. (See 'Q-Calculation' Handout for derivations of equations to predict different connectivity equations.)
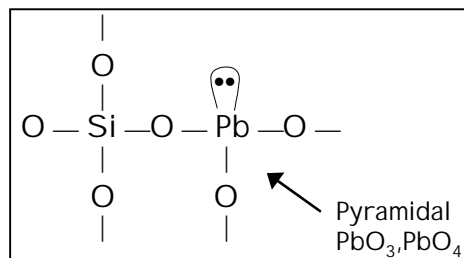

Effects on properties?   Increase in viscosity
                           Increase in elastic modulus
                           Decrease in CTE
                           Increase in Na-diffusion rates (Na^+
                           more weakly bound to AlO_4^- then to Si-NBO^-)

Note that this increase in cross-linking occurs up to $[Al_2O_3] = [R_2O]$; i.e., number of alkalis sufficient to neutralize every AlO_4^-. Further additions of Al_2O_3 ([Al]/[R]>1) have different effects on glass properties, likely because of the formation of tri-coordinated oxygens.

I.3 PbO-Silicate Glasses

Very high PbO-contents, >50 mole% PbO
• Q^1, Q^0 silicates- no connected silicate network

Weak Pb-O bonds (low field strength, large, Pb^{2+} ions): low T_g's
• microelectronic packaging applications

Note: change in structural role for Pb^{2+}:
• low PbO: incorporated into glass network, chemically resistant
• 'fine Pb-crystalwear'
• high-PbO: acts more like a glass modifier; easily leached (esp. acids)
• 'Fiestawear' glazes and orange juice