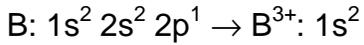## II. Structural Models for B_2O_3

Next to silicates, most technologically (and scientifically) interesting glasses.

B: $1s^2\ 2s^2\ 2p^1 \rightarrow B^{3+}: 1s^2$

- sp^2 hybridization: planar BO_3 triangles

Vitreous B_2O_3: unusual intermediate range structure; linked triangles forming
planar rings: Boroxol Rings.
- Glass possesses some aspects of 'sheet-like' properties (akin to graphite).
  - Strong intra-ring bonds, weak van der Waal's inter-ring bonds
  - T_g (B_2O_3) ~260ºC (2D-network)
  - T_g (SiO_2) ~1200ºC (3D-network)

Boroxol Rings: • very well defined structural unit
                 • unusual because this does not occur in crystalline B_2O_3
                 polymorphs; B_2O_3 glass is *very* difficult to crystallize (probably
                 because of these rings).

Shelby (1997), figure 5-4.

F. L. Galeener, in *Structure of Non-Crystalline Materials* (1982)
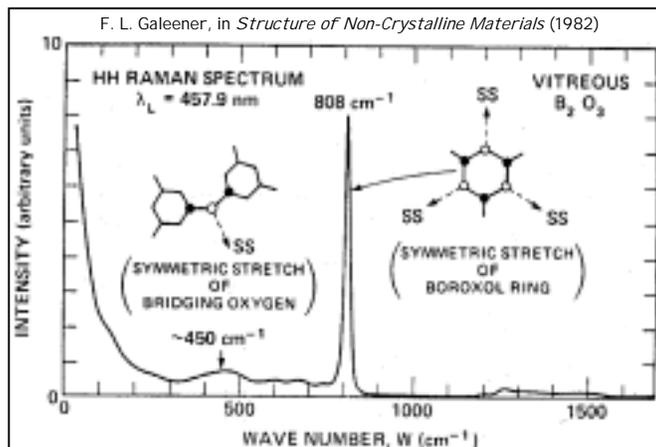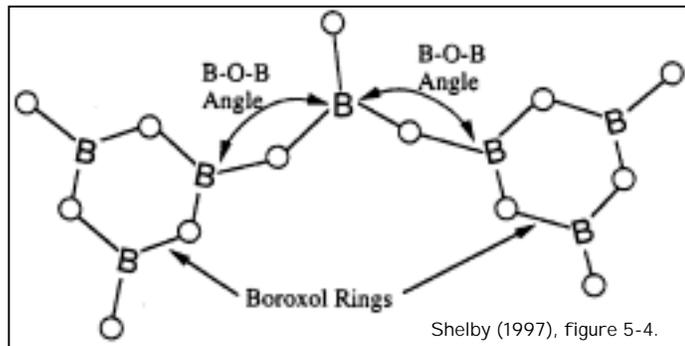
Raman spectroscopy (Shelby): very sharp line (for a glass) means highly ordered
structural element, within amorphous long-range structure- the latter arises
because of distributions in the inter-ring B-O-B bond angles (Shelby fig 5-4).

II.1 Alkali Borate Glasses

B_2O_3 network might be modified by R_2O additions in two ways:

1. NBO formation (like xR_2O (1-x)SiO_2 glasses), or
2. Tetrahedral boron formation (like Al^{3+} added to an alkali silicate)?

What happens when alkali oxide is added to a borate glass?

Nonbridging oxygens form?

Tetrahedral borons form?

Different structures should lead to different trends in properties.

Viscosity data (Shelby figure 6-5) suggests that the network (at least initially) becomes more cross-linked with the addition of alkali oxide to B_2O_3, opposite of the situation with alkali oxide additions to SiO_2.

Shelby (1997), figure 6-5.

xLi$_2$O (1-x)B$_2$O$_3$ glass

'constant viscosity' temperature goes through a maximum

Implication: B[3] + $R_2O \rightarrow$ B[4]
- Increasing fraction of B[4]
- More bridging oxygens added to the network
- **Borate Anomaly**: initial additions of R_2O have opposite effects on the properties and structures of borate and silicate glasses.
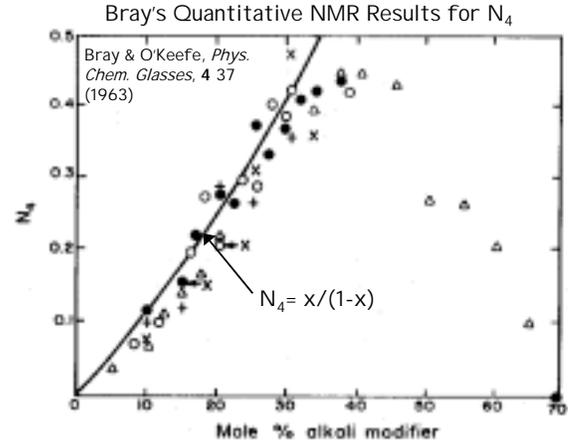
Bray used Nuclear Magnetic Resonance (NMR) to measure the relative concentrations of B[3] and B[4] sites in several series of alkali borate glasses.

Define N_4 = B[4]/B(total)

For xR_2O $(1-x)B_2O_3$ glasses:

   Total # of borons = 2(1-x)
If every R^+ is neutralizes one BO_4^-,
   Total # of B[4] = 2x

Bray's Quantitative NMR Results for N_4

Bray & O'Keefe, *Phys. Chem. Glasses*, **4** 37 (1963)

$N_4 = x/(1-x)$

Mole % alkali modifier

Therefore: **$N_4 = 2x/2(1-x) = x/(1-x)$**

Note that N_4 reaches a maximum near ~30-40 mole% R_2O; viscosity maxes out near ~20-30 mole% R_2O. Further additions cause a decrease in N_4 and a reduction in viscosity. Now what is happening to the glass structure?

At higher R_2O contents, NBO's are formed in a manner similar to the silicates.
   • Fewer network bridging oxygens,
      • Lower viscosity
      • Lower T_g
      • Higher CTE, etc.

Effect of Alkali Addition on Borate Glass Networks
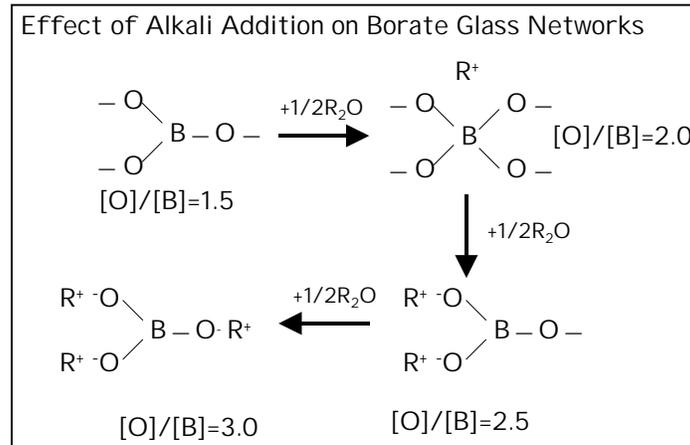
As in alkali borate crystals, these glasses can also possess molecular units- IRO (intermediate range order).

Shelby (1997), figure 5-5.
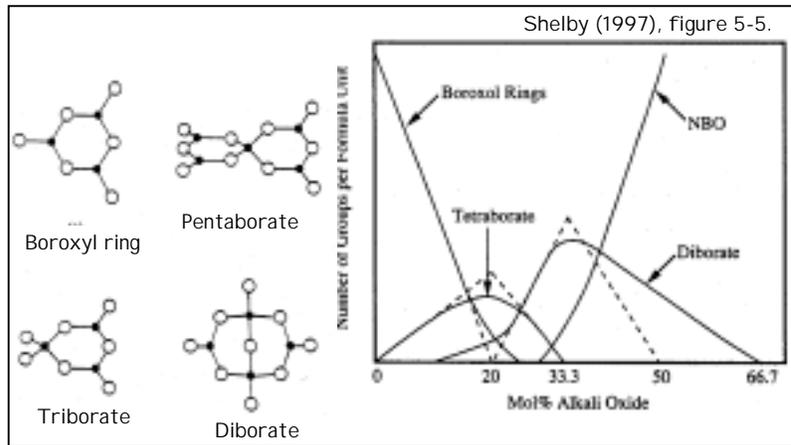
Glass properties are sensitive to changing distributions of these molecular units-leads to complicated relationships between glass properties and structure (e.g., related to why viscosity maximum does not occur at the same composition as the maximum in N_4).

II.2 Aluminoborate Glasses

Shelby describes a simple model in which, like silicate glasses, alkali/alkaline earth oxides stabilize AlO_4 sites and, if $R_2O=Al_2O_3$, only neutral B[3] would be present.
- Result is a highly cross-linked, non-silicate network
  - Applications where silicate chemistry is detrimental
    - Na-vapor lamps
    - Li-battery story

II.3 Borosilicate Glasses

Story:
At the turn of the century, there was a significant problem with the type of glass used to manufacture railroad signal lanterns. The kerosene lamps would heat the glass and, if this relatively high expansion soda-lime glass was then exposed to cold rain, the glass would shatter (and trains would wreck).

Around 1912, Corning researchers (by trial and error) discovered a heat-resistant glass, chemically durable composition based in part on mixtures of sand and borax; trademark name Pyrex, used initially in lanterns and battery acid jars (telephone/telegraphs). Later discovered baking/cooking applications.

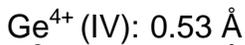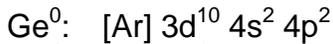Two network forming oxides: B_2O_3 and SiO_2; miscibility issues.
- Adding R_2O will either: create NBO's on the silicate network
                                    convert B[3] $\rightarrow$ B[4]

Overall network description depends on whether or not phase separation occurs (particularly an issue when $R_2O<20$ mole%).

Homogeneous high alkali borosilicate glasses have compositional dependencies similar to the alkali borates; e.g., maximum in N_4, then conversion to B[3]-NBO at higher R_2O. Details depend on SiO_2-contents.

 Note: nice work in the undergrad Physics department at Coe College.

III.   Germanate Glasses

Ge^0:   [Ar] $3d^{10}$ $4s^2$ $4p^2$
Ge^{4+}: [Ar] $3d^{10}$

Ge^{4+} (IV): 0.53 Å
O^{2-} (II):   1.21 Å; r_c/r_a = 0.438, on the tetrahedral/octahedral boundary (0.414)

GeO_2 glass: •tetrahedral 'quartz-like' structure;
                   •Ge-O-Ge bond angle a little smaller than SiO_2;
                   •T_g about 600°C, compared to ~1200°C for SiO_2;
                   •easily made from the melt.

What happens when modifying oxides are added to GeO_2?
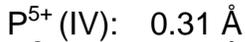

J. E. Shelby, J. Amer. Ceram. Soc., (1974)
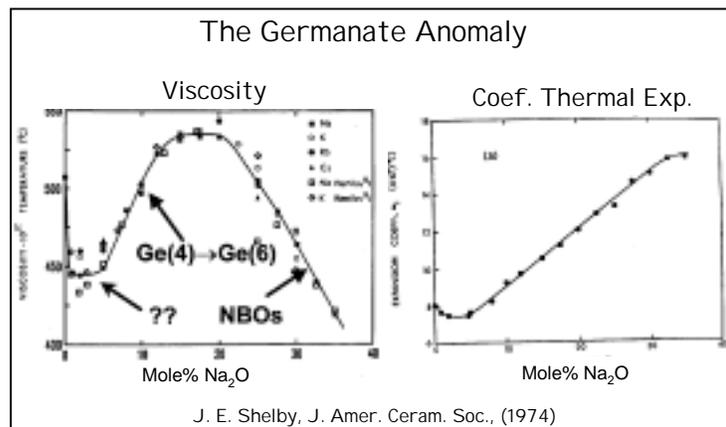
*   Initial additions of R_2O appear to create both NBO's and $(GeO_6)^{2-}$.
*   Above about 5 mole% R_2O, Ge(4)$\rightarrow$Ge(6) dominates properties;
*   Above about 20 mole% R_2O, NBO formation dominates properties.

Shelby talks about elements of IRO controlling properties, although more recent work (e.g., Jain et al.) supports the Ge(6) story.

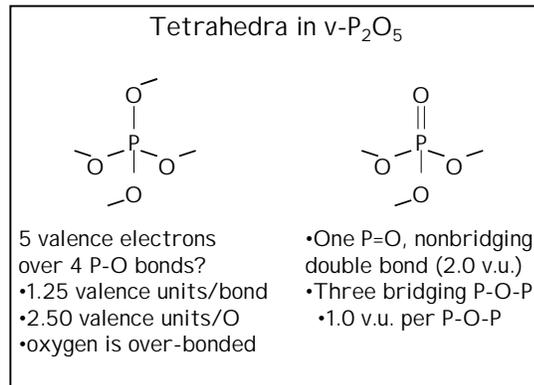Germanate glasses have higher refractive indices than silicates
 • Important constituent in silica fibers:
     • Modifying n for waveguiding
     • More recently, Ge-defects in fibers/films for optical gratings
GeO_2 is pretty expensive; limits applications.

IV.   Phosphate Glasses

P^0:   [Ne] $3s^2$ $3p^3$
P^{5+}:   [Ne]

P^{5+} (IV):   0.31 Å
O^{2-} (II):   1.21 Å; r_c/r_a = 0.256, tetrahedral configuration is preferred

What does a tetrahedron in P_2O_5 look like?
      Extra valence electron compared to Si^{4+} or Ge^{4+}

Tetrahedra in v-P_2O_5

5 valence electrons over 4 P-O bonds?
•1.25 valence units/bond
•2.50 valence units/O
•oxygen is over-bonded

•One P=O, nonbridging, double bond (2.0 v.u.)
•Three bridging P-O-P
•1.0 v.u. per P-O-P

Three-dimensional P_2O_5 network? T_g ~400°C (v-B_2O_3~260°C, v-SiO_2~1200°C)

P_2O_5 is very reactive: an excellent desiccant
                        related to the electron asymmetry of the PO_4 tetrahedron
                        not very useful (despite a deep UV-edge).

What happens when you add a modifying oxide??

Q^3 Network $\xrightarrow{+R_2O}$ Q^2 Chains
(1NBO/P)   (2NBO's/P)
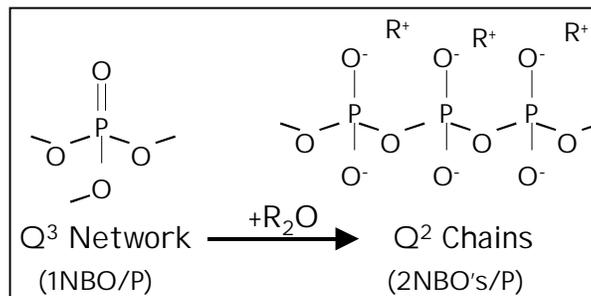
Metaphosphate glasses: 50 mole% R_2O (or RO); easy to prepare from melt
                             100-500 tetrahedra chains;
                             Properties are sensitive to ionic bonds between chains
                             Chemically durability is poorer than silicate glasses
                             used as water softeners, mineral carriers for agricultural
                             and biomedical applications, etc.

Oxygen Bonding in Simple Phosphate Glasses

> For xR_2O $(1-x)P_2O_5$ Glasses:
> total # of oxygen = $x + 5(1-x) = 5-4x$
> #NBO =   # due to R^+ + the extra due to P^{5+}
> $2x + 2(1-x) = 2$
> fraction of NBO's = $2/(5-4x)$
> fraction of BO's = 1-frac. NBO's = $(3-4x)/(5-4x)$
>
> for $0 \leq x \leq 0.50$: frac Q^2 = (#alkali)/(#p_tetrahedra)
> $2x/2(1-x) = x/(1-x)$

Properties can be modified by alumina additions (Launch the ALSG Story)
- Alumina provides chemically stable cross-links between P-chains

More recently, specialty phosphate glasses with much smaller phosphate anions (lots of Q^1, Q^0 species) have been developed.
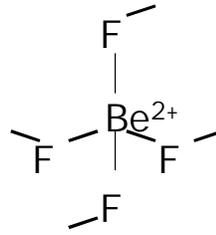- Fe-phosphates (Q^1 stoichiometry)- nuclear waste encapsulants
- Zn/Sn-pyrophosphates: specialty sealing applications

V.   Halide Glasses

V.1 BeF_2 is isostructural to SiO_2:

BeF_2	SiO_2
$r(Be^{2+}) = 0.41$ Å	$r(Si^{4+}) = 0.40$ Å
$r(F^-) = 1.15$ Å	$r(O^{2-}) = 1.21$ Å
$r_c/r_a = 0.36$	$r_c/r_a = 0.33$
F.S.* = 1.32 Å^{2-}	F.S.* = 5.19 Å^{2-}

*$FS = z_a z_c/(r_c+r_a)^2$

BeF_2 has a high viscosity at liquidus; good glass forming tendency.
- Bridging Fluoride Bonds
- Adding RF creates nonbridging fluorides (analogous to silicates).
- Shelby points out phase separation into BeF_2-rich & RF-rich phases

V.2 $ZnCl_2$ $r(Zn^{2+}) = 0.74$ Å
                   $r(Cl^-) = 1.67$ Å
                   $r_c/r_a = 0.44$; tetrahedral, low FS (0.83 Å^{2-}) structure

- Modest viscosity at liquidus (more difficult to avoid crystallization)
- Poor durability; few applications (IR transmission?)

V.3   Heavy Metal Fluorides
- Discovered in 1974. ZrF_4 used as flux for fluoride crystal growth studies. Melts didn't crystallize as expected- new glass forming system discovered as a result.
- Highly ionic structures; 30-70 mole% ZrF_4
   - $r_c/r_a \sim 0.7$; structures based on ZrF_7, ZrF_8 polyhedra (non-Zachariasen)

Phifer and Angell structure picture	IR Transmittance curves

Modified with other heavy metal fluorides: BaF_2, LaF_3, AlF_3 (to promote glass formation)- 'ZBLA' compositions for IR transmittance.
- Transmit to longer wavelengths- lower intrinsic loss due to Rayleigh scattering
   - At one time, ZBLA glasses pegged to replace SiO_2 for long distance optical communications
      - Problems: prone to crystallization (low viscosity melts)
                Relatively poor durability

VI.   Chalcogenide Glasses

- Based on elements 'from copper' minerals: S, Se, Te
  - Elements form glasses by themselves on cooling
    - Form chains: [-S-S-S-]-; akin to organic polymers, metaphosphates
  - Combined with group IV, V elements like Si, Ge, Sn, As, Sb

Group IV, V elements cross-link the chalcogenide chains:
- (8-n) rule for co-ordination: n is the # of outer shell electrons
  - Ge^0:   [Ar] $3d^{10} 4s^2 4p^2$; n=4, CN=(8-4)=4
  - As^0:   [Ar] $3d^{10} 4s^2 4p^3$; n=5, CN=(8-5)=3
  - Se^0:   [Ar] $3d^{10} 4s^2 4p^4$; n=6, CN=(8-6)=2

- Si, Ge, Sn: CN=4
- P, As, Sb: CN=3
- S, Se Te: CN=2
  - Average CN=Σ(at frac)(CN)
    - As_2Se_3: avg(CN) = 0.4(3)+0.6(2) = 2.4
    - Properties (viscosity, density, etc.) depend on average CN

Shelby Figure 5-6

Primary applications?
- Photoconductivity--xerography
- IR-transmission (glasses are black, but transparent to IR)
  - CO_2 fiber lasers (10.6 μm)
- Made in sealed ampoules, high purity raw materials to avoid O-contamination

Chalcohalide glasses contain halide elements:Te_3Cl_2, Te_3Br_2Se, etc.
 - 'TeX' glasses, where 'X' is a halide
  - 'TeXAs'
  - Halides are chain terminators; very fluid and low T_g's
  - Greater IR transparency than chalcogenides; poorer durability, more prone to crystallization

VII.   Organic Glasses
- Long chain polymers

Glassy Metals
- Metal (Fe, Ni, Pd)-Metalloid (P, Si, B) eutectic compositions
  - Electrical, magnetic, optical properties of metals, but also possess glass transformation behavior and amorphous structure (dense random packing of spheres).
    - No grain boundaries: better corrosion, better mechanical properties
  - Metalloids occupy interstices, interfere with reorganization of metal melt into crystalline structure
  - $Pd_{80}Si_{20}$, $Ni_{80}P_{20}$, $Fe_{40}Ni_{40}P_{14}B_{6,}$ etc.

- Generally manufactured as ribbon, more recent alloys have high enough viscosities at liquidus to cast bulk samples

Golf Club Picture
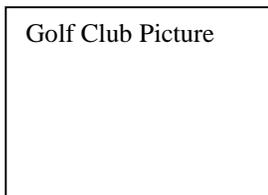
Commercial Compositions

Types of Commercial Compositions (Varshneya, Table 1-1):

Varshneya
Table 1-1

See also "Perspectives on the History of Glass Composition," by C. R. Kurkjian and W. R. Prindle, *J. Amer. Ceram. Soc.*, 81[4] 795 (1998).

- **High silica**
  - Fused quartz/fused silica (sand); CVD silica from $SiCl_4$-flame hydrolysis (1000 ppm OH^-, reduced to 5 ppm in 'dry' plasma torches); sol-gel process (low temperature hydrolysis and condensation of Si-precursors (e.g., Tetraethyl orthosilicate)
  - Vycor: invented at Corning in 1930's (heat treatment experiments on Na-borosilicate glasses).

- **Soda-Lime Silicate** (largest by volume)
  - SiO_2 is the excellent glass former;
  - Na_2O is added as a flux;
  - CaO is added because of the poor durability of binary Na-silicates; (glass formation is difficult in the binary CaO-silicate system).

- Typical SLS compositions based on $Na_2O \bullet CaO \bullet 6SiO_2$ (or about 15-18 wt% Na_2O 10wt% CaO(w/ MgO), 72-75 wt% SiO_2. Typically also contain ~1 wt% Al_2O_3 to suppress devitrification and improve durability.
    - Basic composition set in 1800's
    - Improvements in melting technology (higher temperatures, better refractories) support more recent trends to lower alkali, higher lime (and so more durable) glasses.
        - Actual compositions depend on relative costs of raw materials- can vary by a couple of wt% without much variation in glass properties.

- **Borosilicates**- chemical stability, lower expansion applications
    - Railroad brakeman's problem: Nonex (non-expansion) Pb-borosilicate; Pyrex becomes the PbO-free composition
        - Pyrex: lowest liquidus temperature for any high silica composition
        - Other low-expansion borosilicates used for Mt. Palomar mirror blank (200-inch diameter casting)
            - Extremely low cooling rate required low liquidus temperature to avoid devitrification.
        - Boron is a relatively expensive raw material (compared to SLS)

- **Pb-silicates**- high refractive index tableware; low temperature solder glasses have higher PbO contents

- **Aluminosilicates**- alkali-free, durable compositions
    - **E-glass** (electrical insulation applications); Lime-aluminoborosilicate
        - Based on (wt%) 23.3% CaO 14.5% Al_2O_3 62.2% SiO_2 eutectic
        - Superior resistance to chemical attack
        - Continuous fiber technology
    - **S-glass** (20% higher strength than E-glass)
        - Borate-free; greater mechanical modulus for composites
        - Requires high fiberization temps. (1500-1600°C); no fluxes