II. Structural Models for $\text{B}_2\text{O}_3$

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

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

- \text{sp}^2 \text{ hybridization: planar BO}_3 \text{ triangles}

Vitreous $\text{B}_2\text{O}_3$: 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
- $T_g$ ($\text{B}_2\text{O}_3$) $\sim$260ºC (2D-network)
- $T_g$ ($\text{SiO}_2$) $\sim$1200ºC (3D-network)

Boroxol Rings:
- very well defined structural unit
- unusual because this does not occur in crystalline $\text{B}_2\text{O}_3$ polymorphs; $\text{B}_2\text{O}_3$ glass is very difficult to crystallize (probably because of these rings).

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)?

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 $SiO_2$.


- 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 $N_4 = B[4]/B(\text{total})$

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] = $2x$

Therefore: $N_4 = \frac{2x}{2(1-x)} = \frac{x}{1-x}$

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.

As in alkali borate crystals, these glasses can also possess molecular units- IRO (intermediate range order).
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 \( \text{AlO}_4 \) sites and, if \( \text{R}_2\text{O}=\text{Al}_2\text{O}_3 \), only neutral \( \text{B}[3] \) 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: \( \text{B}_2\text{O}_3 \) and \( \text{SiO}_2 \); miscibility issues.
- Adding \( \text{R}_2\text{O} \) will either: create NBO’s on the silicate network
- convert \( \text{B}[3] \rightarrow \text{B}[4] \)

Overall network description depends on whether or not phase separation occurs (particularly an issue when \( \text{R}_2\text{O}<20 \) 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

- **$Ge^6$:** $[Ar]$ $3d^{10}$ $4s^2$ $4p^2$
- **$Ge^{4+}$:** $[Ar]$ $3d^{10}$

- **$Ge^{4+}$ (IV):** 0.53 Å
- **$O^2$- (II):** 1.21 Å; $r_{o}/r_{a} = 0.438$, 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 $GeO_2$?

- 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**

P⁰: \([\text{Ne}]\) 3s² 3p³  

P⁵⁺: \([\text{Ne}]\)

P⁵⁺ (IV): 0.31 Å  
O²⁻ (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 Si⁴⁺ or Ge⁴⁺

Three-dimensional \(P_2O_5\) network? \(T_g \sim 400°C\) (\(\nu\)-B₂O₃ \(\sim 260°C\), \(\nu\)-SiO₂ \(\sim 1200°C\))

\(P_2O_5\) is very reactive: an excellent desiccant  
related to the electron asymmetry of the PO₄ tetrahedron  
not very useful (despite a deep UV-edge).

What happens when you add a modifying oxide??

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-fraction NBO's = $(3-4x)/(5-4x)$

For $0 \leq x \leq 0.50$: fraction $Q^2 = (#\text{alkali})/(#\text{p\_tetrahedra})$

\[
\frac{2x}{2(1-x)} = \frac{x}{(1-x)}
\]

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$_2$:

<table>
<thead>
<tr>
<th>BeF$_2$</th>
<th>SiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>r(Be$^{2+}$) = 0.41 Å</td>
<td>r(Si$^{4+}$) = 0.40 Å</td>
</tr>
<tr>
<td>r(F$^{-}$) = 1.15 Å</td>
<td>r(O$^{2-}$) = 1.21 Å</td>
</tr>
<tr>
<td>$r_c/r_a = 0.36$</td>
<td>$r_c/r_a = 0.33$</td>
</tr>
<tr>
<td>F.S.$^*$ = 1.32 Å$^2$</td>
<td>F.S.$^*$ = 5.19 Å$^2$</td>
</tr>
</tbody>
</table>

*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)

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$_0^0$: [Ar] 3d$^{10}$ 4s$^2$ 4p$^2$; n=4, CN=(8-4)=4
  - As$_0^0$: [Ar] 3d$^{10}$ 4s$^2$ 4p$^3$; n=5, CN=(8-5)=3
  - Se$_0^0$: [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$_2$Se$_3$: avg(CN) = 0.4(3)+0.6(2) = 2.4
- Properties (viscosity, density, etc.) depend on average CN

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$_3$Cl$_2$, Te$_3$Br$_2$Se, 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
  - $\text{Pd}_{80}\text{Si}_{20}$, $\text{Ni}_{80}\text{P}_{20}$, $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_{6}$, etc.

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

Commercial Compositions

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

- 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)
  - $\text{SiO}_2$ is the excellent glass former;
  - $\text{Na}_2\text{O}$ is added as a flux;
  - $\text{CaO}$ 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 Na₂O•CaO•6SiO₂ (or about 15-18 wt% Na₂O, 10wt% CaO(w/ MgO), 72-75 wt% SiO₂. Typically also contain ~1 wt% Al₂O₃ 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% Al₂O₃ 62.2% SiO₂ 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