MIT 3.071
Amorphous Materials

2: Classes of Amorphous Materials

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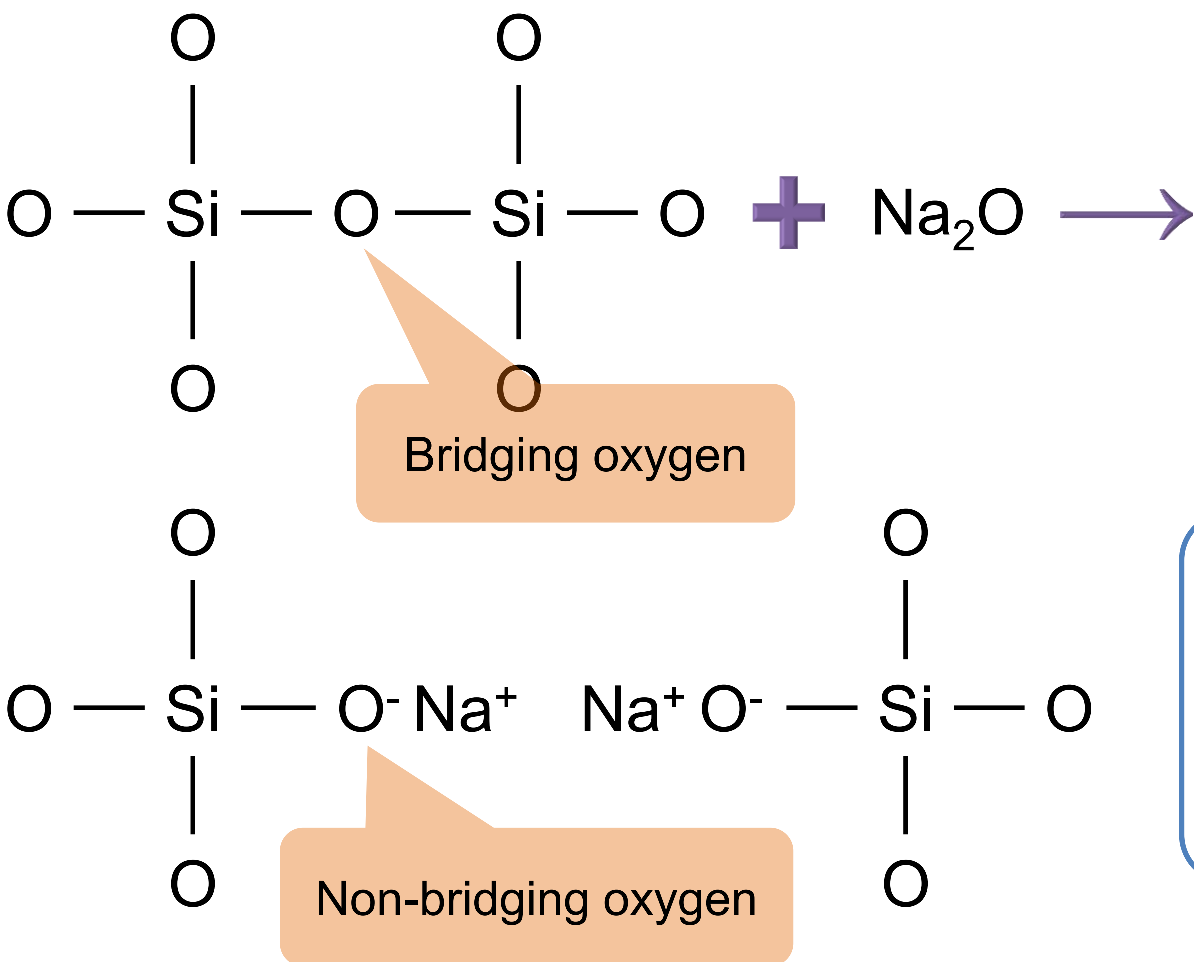
Network formers, modifiers and intermediates

- Glass network formers
  - Form the interconnected backbone glass network
- Glass network modifiers
  - Present as ions to alter the glass network
  - Compensated by non-bridging oxygen (NBO) in oxide glasses
  - Usually reduce glass network connectivity
- Intermediates
  - Can function as network formers or modifiers depending on glass composition

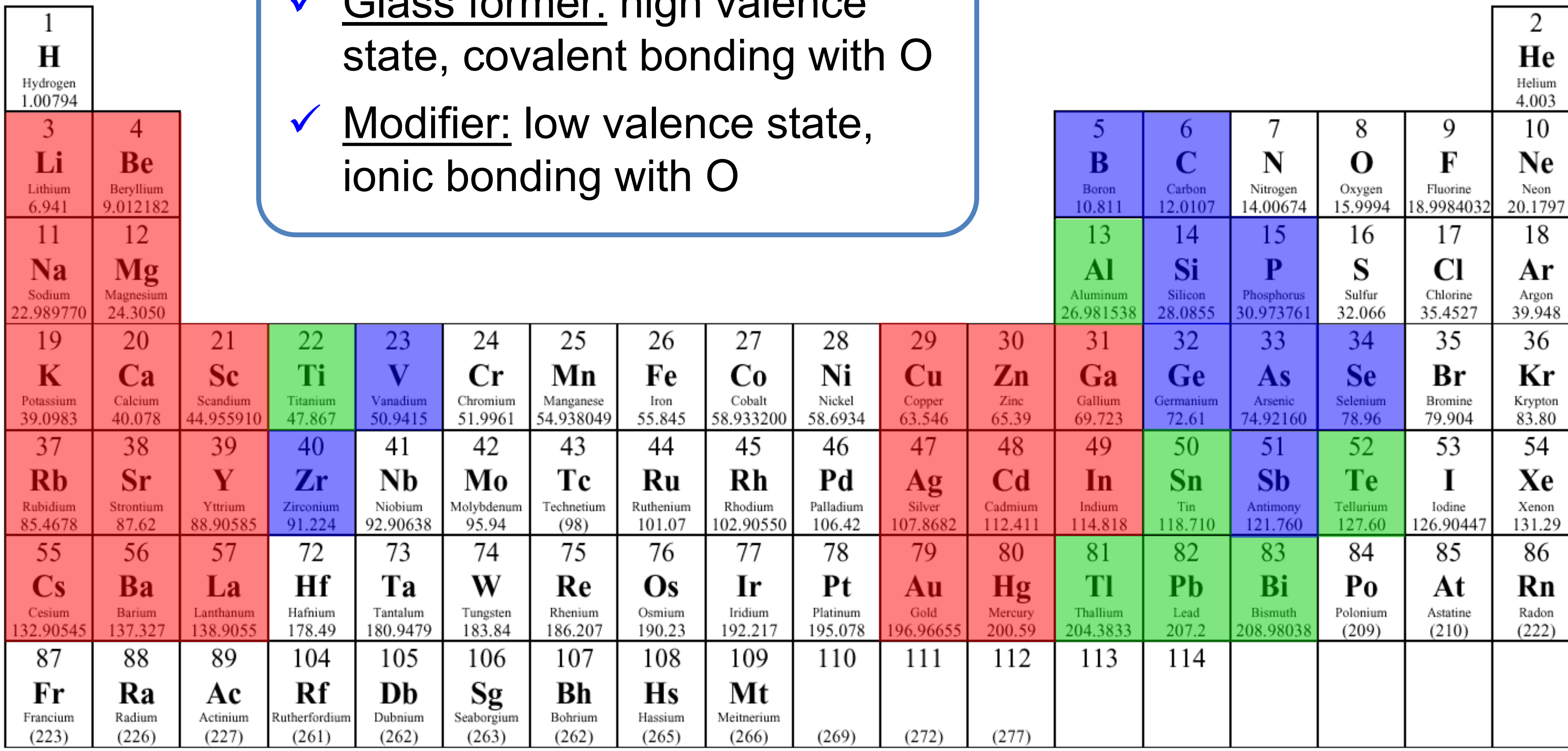
Network formers, modifiers and intermediates



Silicon:
glass former

Sodium:
network modifier

- ✓ <u>Glass former:</u> high valence state, covalent bonding with O
- ✓ <u>Modifier:</u> low valence state, ionic bonding with O



Network modifiers

Glass formers

Intermediates

Silica glass (SiO_2)

- A 3-D glass network predominantly consisting of corner-sharing SiO_4 tetrahedra interconnected by bridging oxygen (BO)
- High network connectivity: high softening point, low diffusion coefficient, small coefficient of thermal expansion (CTE)

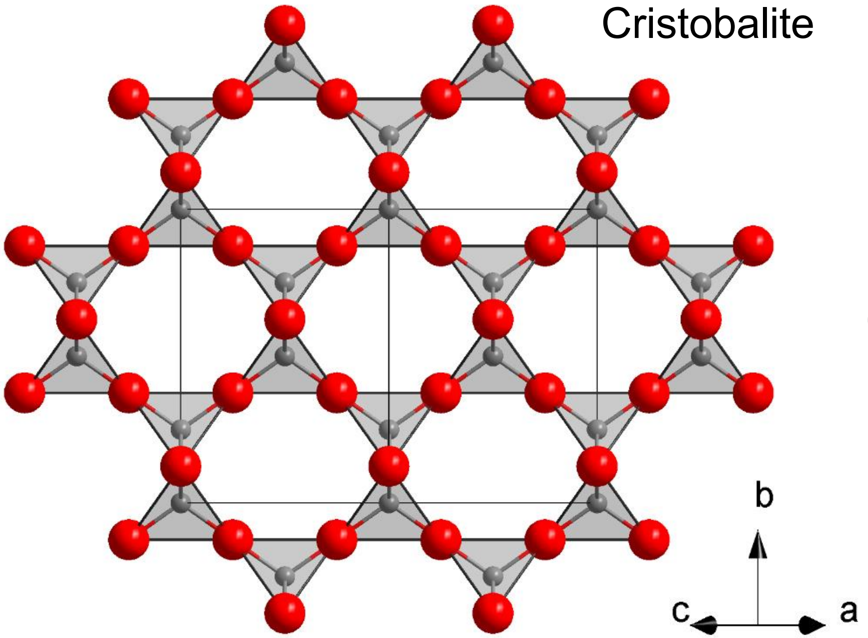
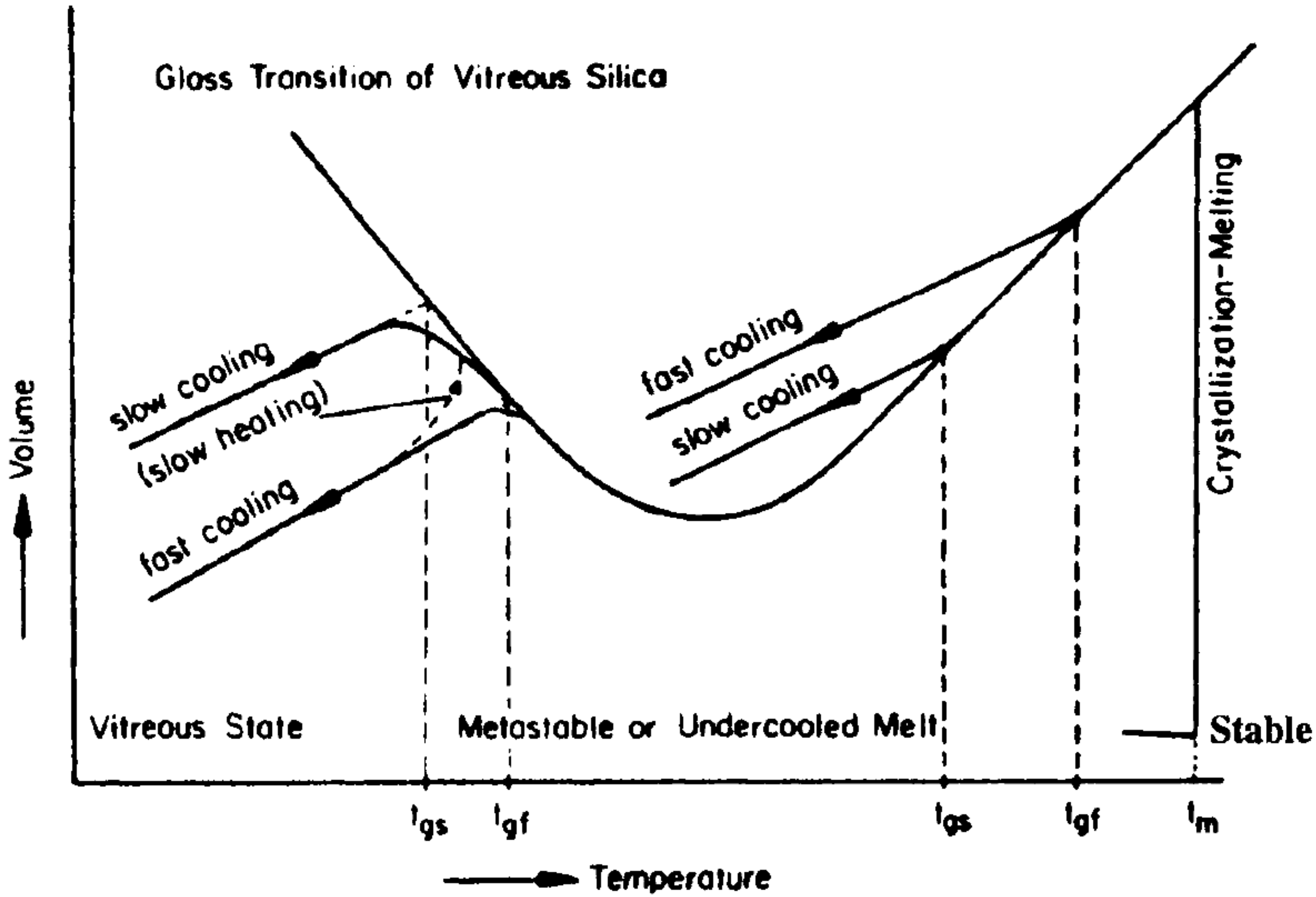


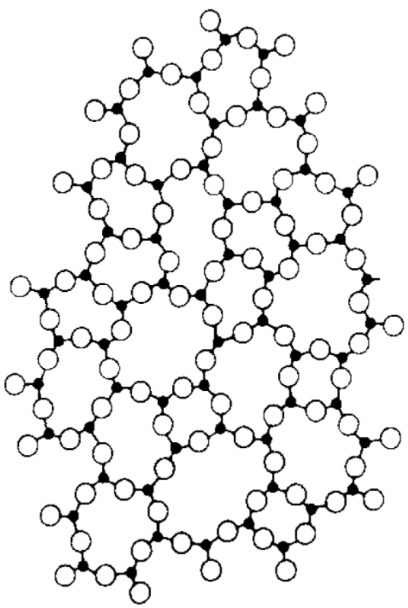
Image of vitreous silica removed due to copyright restrictions.

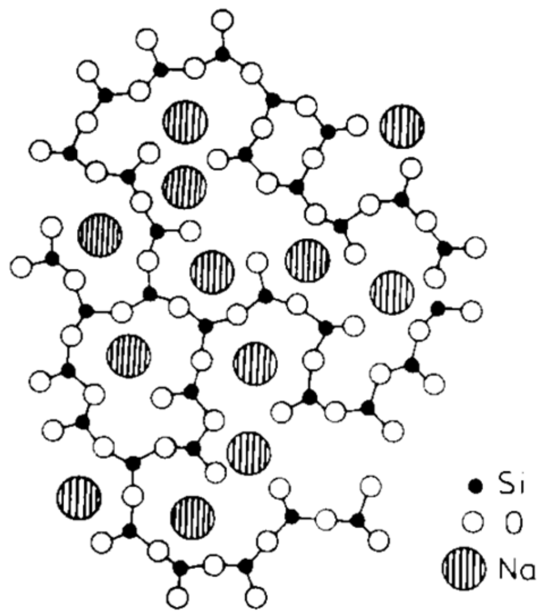
Volume anomaly in silica glass

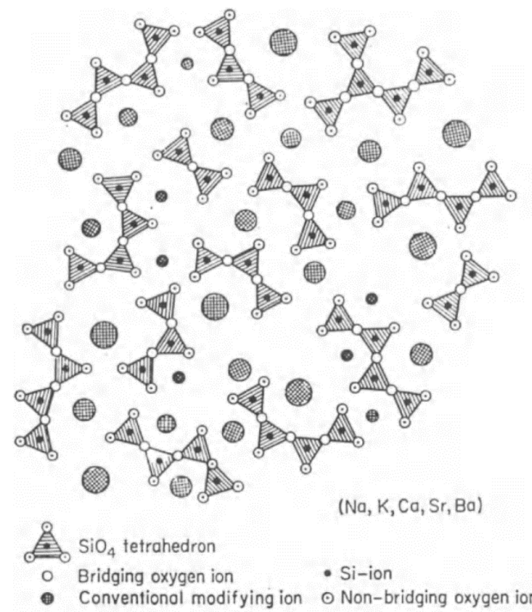


Alkali silicate glass

- Each alkali ion creates one non-bridging oxygen
- Reduced network connectivity: viscosity decreases (compared to silica at the same T), diffusion coefficient and CTE increases
- Increased ionic conductivity, reduced chemical resistance





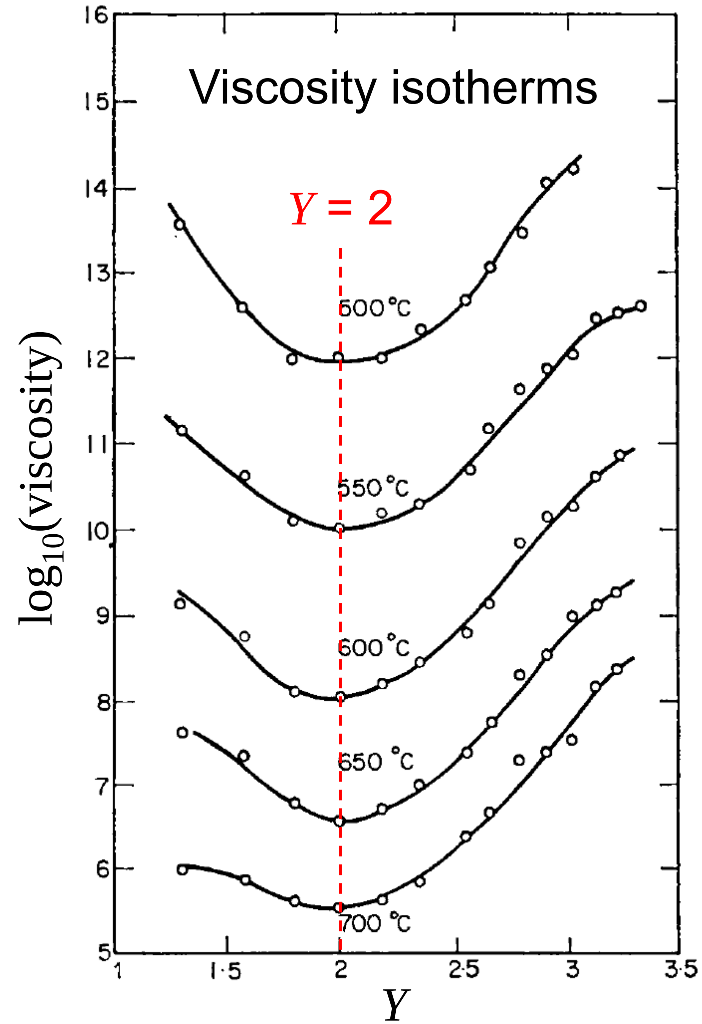


Invert glass

Increasing alkali concentration

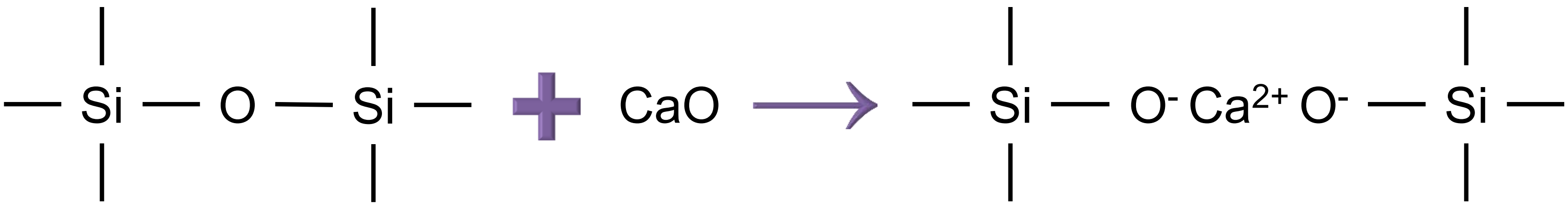
Structural determination in alkali silicate glass

- Y : the average number of corners shared per SiO_4 tetrahedron
- In a glass with molar composition: $x\ Na_2O \cdot (1-x)\ SiO_2$
  - Number of NBO per mole: $2x$
  - Number of BO per mole: $2-3x$
  - Number of corners shared per mole: $(2-3x) \times 2 = 4-6x$
  - Number of tetrahedra per mole: $1-x$
  - $Y = (4-6x) / (1-x)$
- Onset of inverted glass structure: $Y = 2$, $x = 0.5$

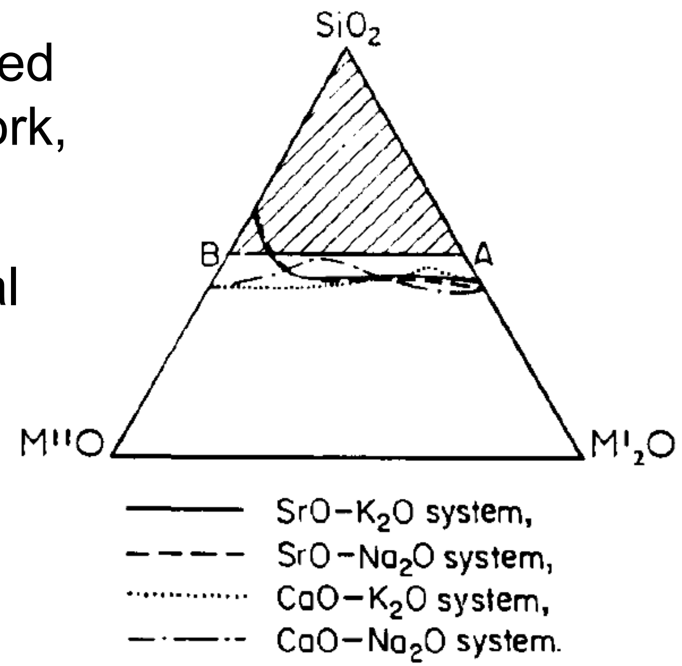


Alkali-alkaline earth-silicate glass

- Each alkaline earth ion creates two NBOs

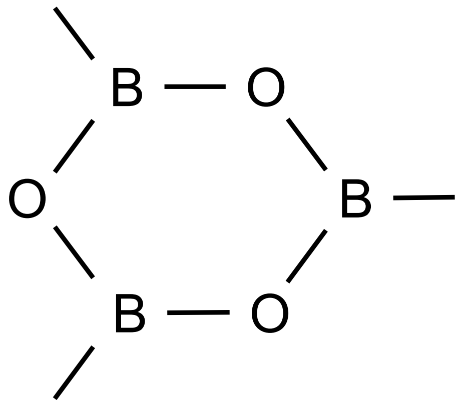


- Increased network connectivity compared to alkali silicates: stabilized glass network, improved chemical resistance
- Approximate composition of commercial soda-lime glass (window glass):
  - $16Na_2O{\cdot}10CaO{\cdot}74SiO_2$

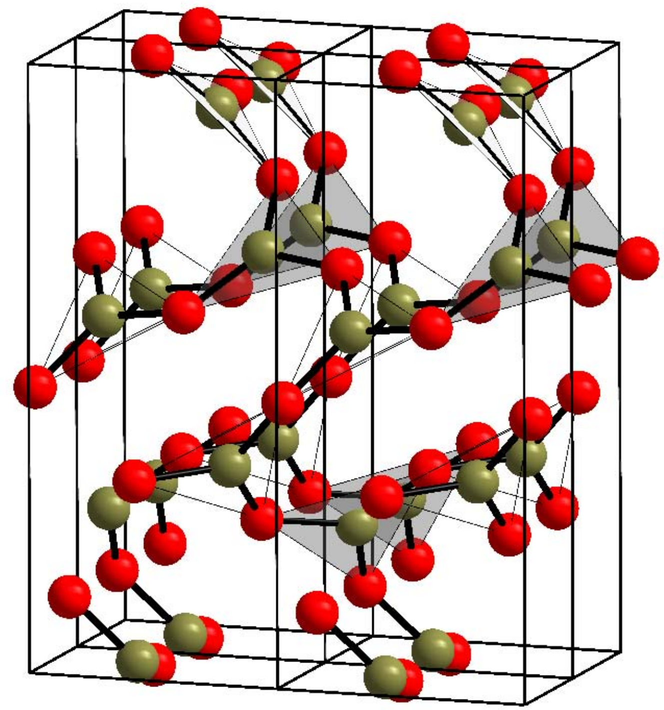


Borate glass

- B_2O_3: the glass former consisting of corner-sharing BO_3 triangles connected by bridge oxygen



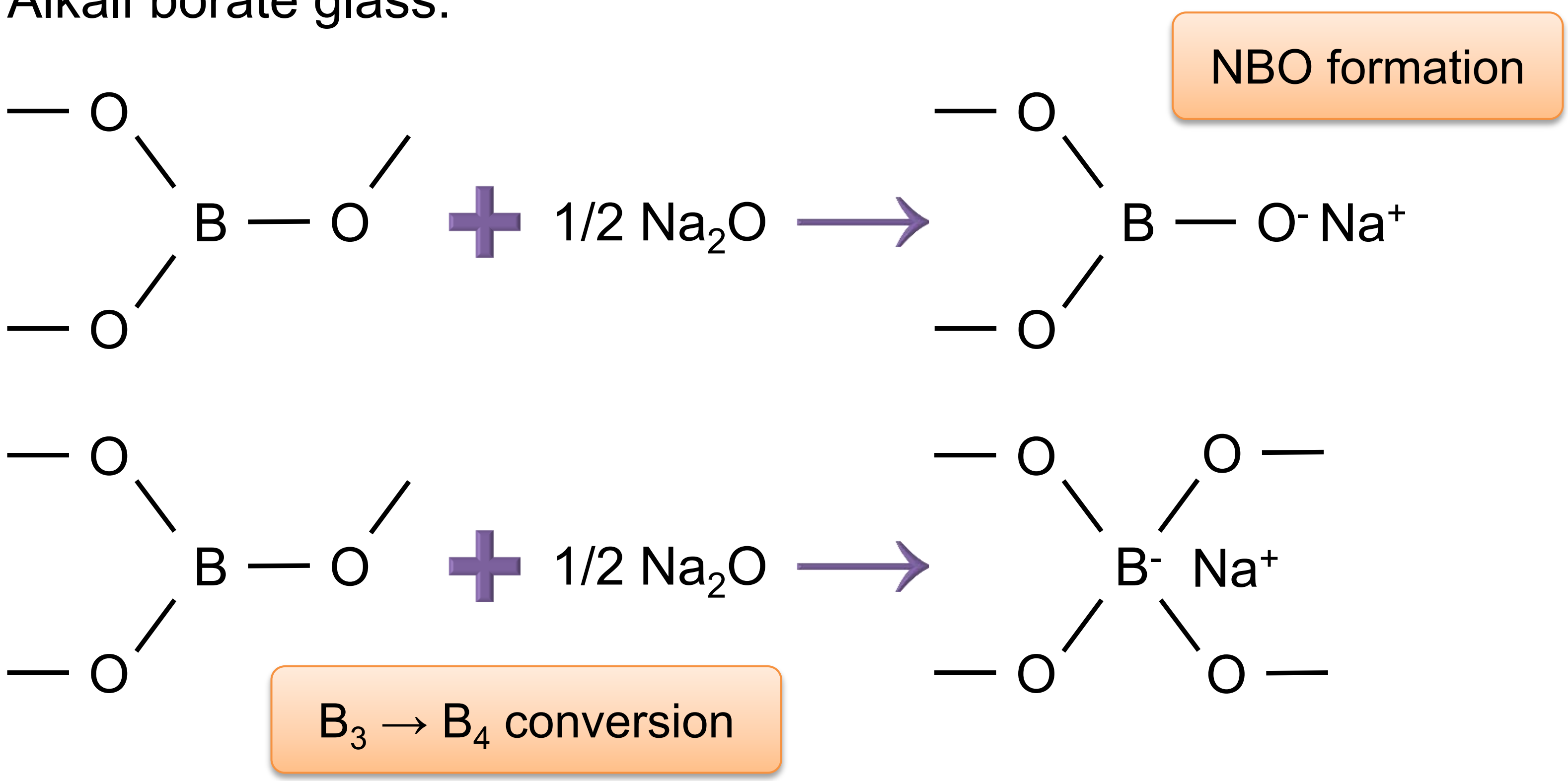
Boroxol rings: basic structural unit in boric oxide glass



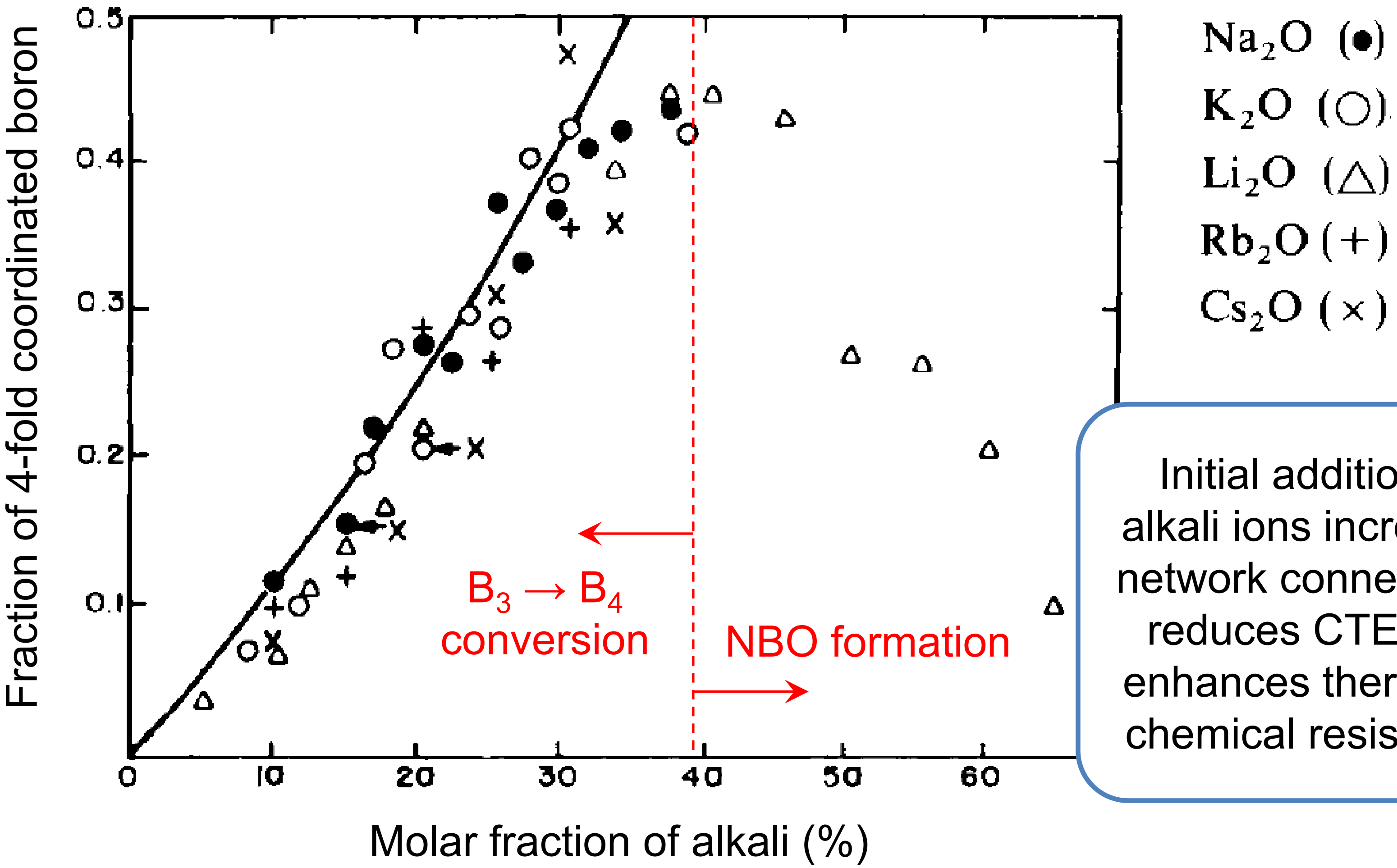
B_2O_3 crystal

Borate glass

- B_2O_3: the glass former consisting of corner-sharing BO_3 triangles connected by bridge oxygen
- Alkali borate glass:

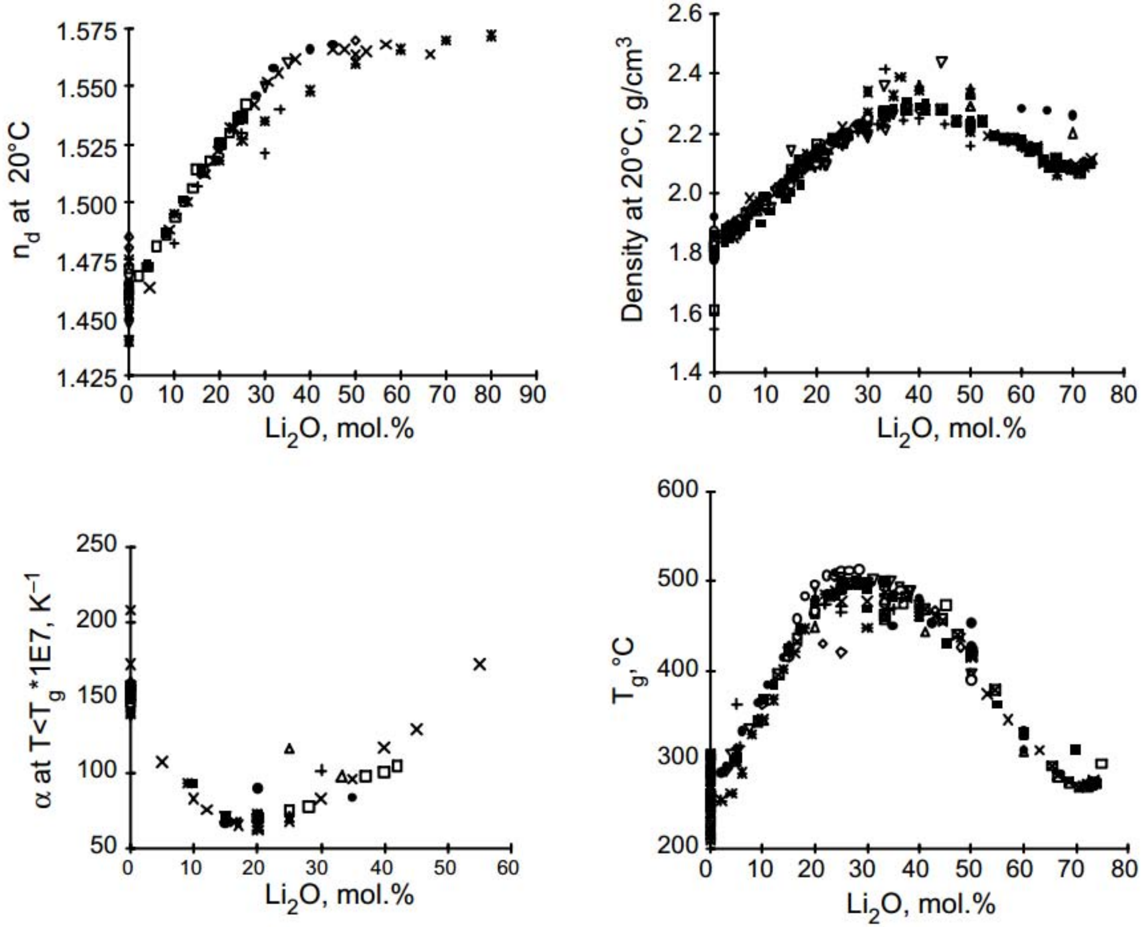


The Boron anomaly



Initial addition of alkali ions increases network connectivity, reduces CTE and enhances thermal & chemical resistance

Various properties of lithium borate glass



J. Non-Cryst. Sol. **351**, 1103-1112 (2005).

More than two structural transformations contribute to the boron anomaly

Further reading: Shelby Ch. 5

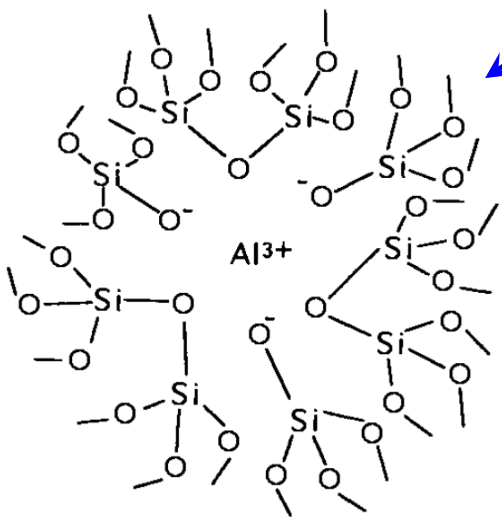
(Alkali) borosilicate glass

- Borosilicate glass: $x\,M_2O \cdot y\,B_2O_3 \cdot (1 - x - y)\,SiO_2$
  - SiO_2 and B_2O_3 : glass formers
  - Alkali ions (M^+) converts B_3 to B_4 states (when $x / y < 0.5$)
  - Each additional alkali ion creates one NBO (when $x / y > 0.5$)
- The original Pyrex™ recipe: $4Na_2O \cdot 13B_2O_3 \cdot 2Al_2O_3 \cdot 81SiO_2$

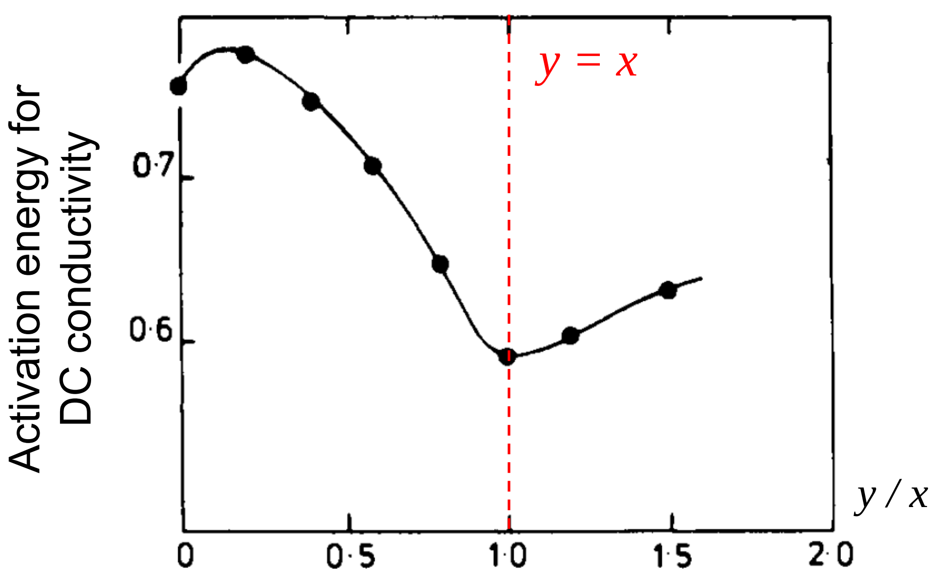
Space shuttle tile coating

(Alkali) aluminosilicate glass

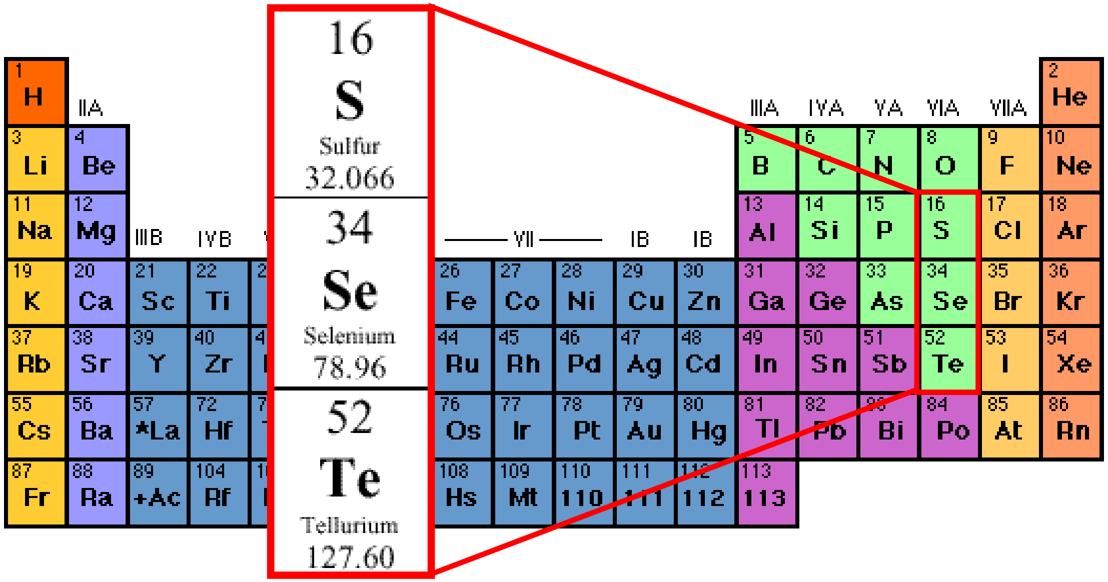
- Aluminosilicate glass: x $M_2O \cdot y\, Al_2O_3 \cdot (1 - x - y)\, SiO_2$
  - SiO_2 : glass former
  - Al functions as a glass former in the form of AlO_4 groups (when $x > y$)
  - Each excess Al atom creates three NBOs (when $x < y$)



Al^{3+} in an oxygen octahedron



Chalcogenide glass (ChG)

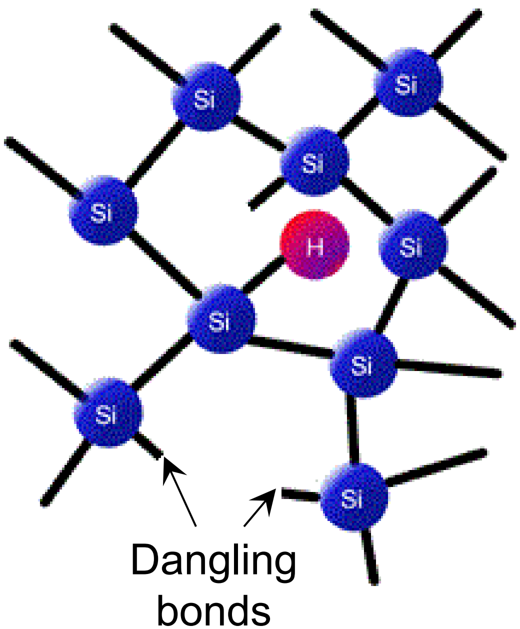


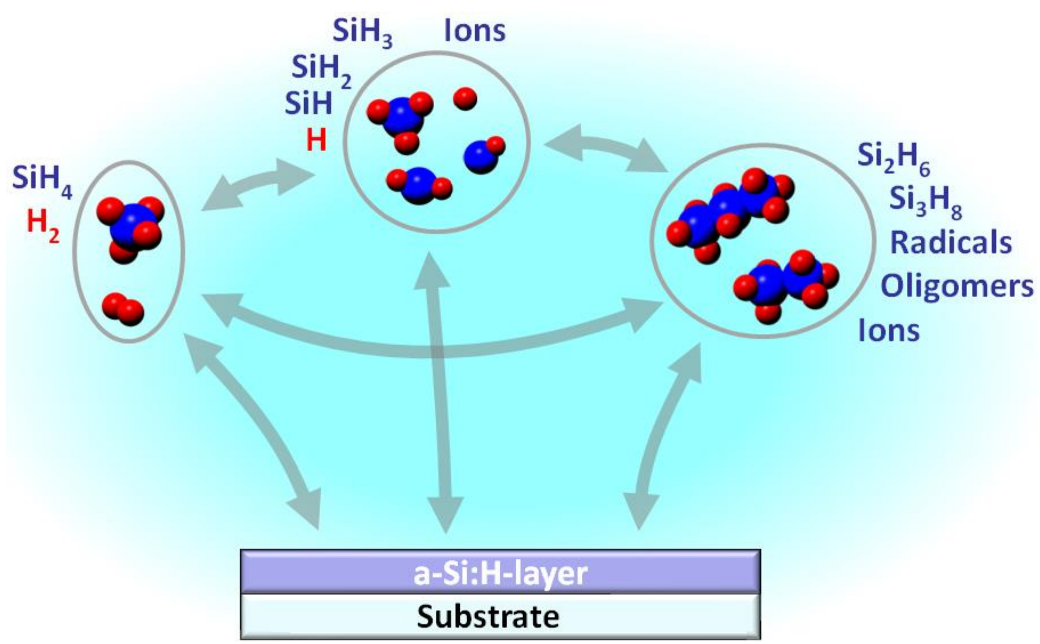
ACerS Bull. **94**, 24-29 (2015).

- Reduced mechanical strength
- Low softening temperature
- Low phonon energy (infrared transparency)
- Enhanced optical (Kerr) nonlinearity

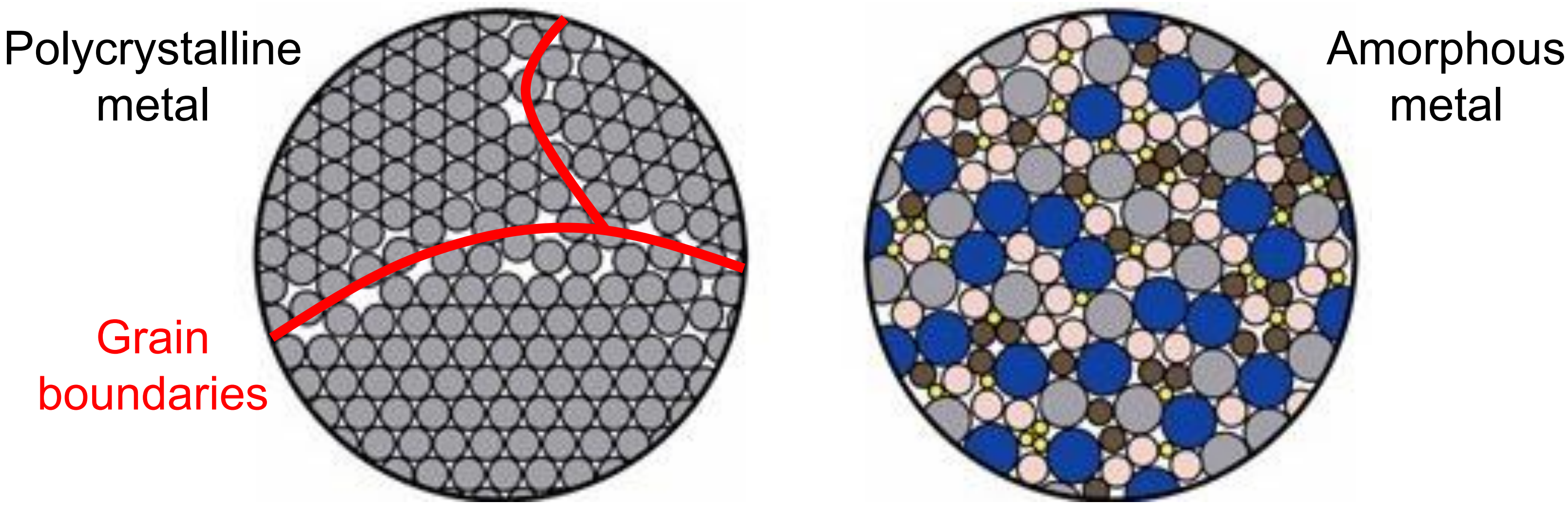
Amorphous semiconductors

- Tetrahedral glasses
  - a-Si, a-Ge, a-Si:H (hydrogenated amorphous silicon)
- Vapor deposition: plasma enhanced chemical vapor deposition (PECVD), sputtering, electron beam evaporation





Metallic glass (amorphous metal, glassy metal)



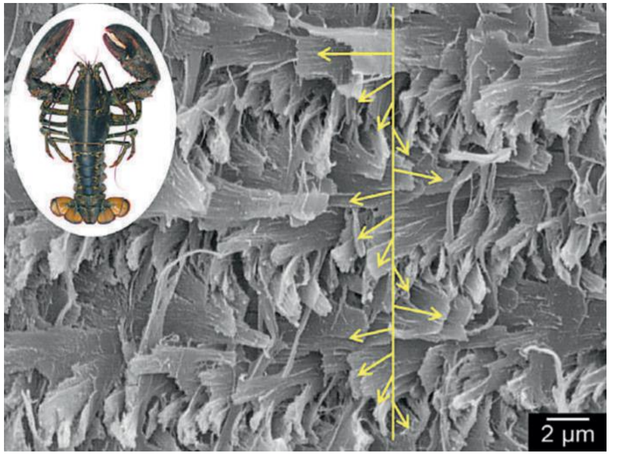
- Inoue's empirical rules for bulk metallic glass (BMG) formation
  - Multicomponent systems consisting of three or more elements
  - Significant difference in atomic size ratios (> 12%)
  - Negative enthalpy of mixing

Other glass groups and glass formers

- Phosphate glass: P_2O_5
- Heavy metal oxide (HMO) and transition metal oxide glass
  - TeO_2, PbO, Bi_2O_3, V_2O_5, TiO_2, etc.
- Halide glass and alloys
  - e.g. ZBLAN: **Z**rF_4-**B**aF_2-**L**aF_3-**A**lF_3-**N**aF
  - Chalcohalide, oxyhalide, etc.
- Amorphous minerals
  - Opal, biominerals

and many others…

Amorphous calcium carbonate in lobster carapace



“The Formula for Lobster Shell,” Max Planck Research

Representation of glass composition

- In oxide glasses, the convention is to list the glass network modifiers in increasing valence order ending with glass network formers
  - Example: $K_2O \cdot CaO \cdot 5SiO_2$
  - In mole fraction: $14.3K_2O \cdot 14.3CaO \cdot 71.5SiO_2$
  - By weight: $20.9K_2O \cdot 12.4CaO \cdot 66.7SiO_2$ (wt%)
- In metallic glasses, the listing is usually done in decreasing order of content
  - Example: $Zr_{41.2}Be_{22.5}Ti_{13.8}Cu_{12.5}Ni_{10.0}$ (Vitreloy-1)

Summary

- Glass formers, network modifiers, and intermediates
- Silicate glass chemistry
  - Corner-sharing tetrahedra
  - Bridging and non-bridging oxygens
  - Different modifiers: alkali, alkali earth
- Borates and boron anomaly
- Impact of network connectivity on glass properties
- Other glass systems
  - Chalcogenides: weak bonds
  - Tetrahedral glasses: passivation of dangling bonds
  - Amorphous metals: w/o grain boundaries

Summary of oxide glass chemistry

	SiO_2 (silicate)	B_2O_3 (borate)
No modifier	Structural unit: SiO_4 No NBOs, low or negative CTE, high softening point, low diffusivity	Structural unit: BO_3 No NBOs, corrugated layered structure
Alkali oxide	Each ion creates 1 NBO; large CTE, low softening point, poor chemical durability, ionic conductivity	Each ion creates 1 B_4 group or 1 NBO; extremum in glass properties (boron anomaly)
Alkaline earth oxide	Each ion creates 2 NBOs; similar effects as alkali ions although some network connectivity is preserved	Each ion creates 2 B_4 groups or 2 NBOs; extremum in glass properties (boron anomaly)
Alumina (Al_2O_3)	Each ion creates 3 NBOs; in the presence of alkali ions $Al_3 \rightarrow Al_4$ conversion occurs	B_2O_3 and Al_2O_3 both serve as glass formers; glass is stable only with high B_2O_3 content