MIT 3.071
Amorphous Materials

2: Classes of Amorphous Materials

Juejun (JJ) Hu

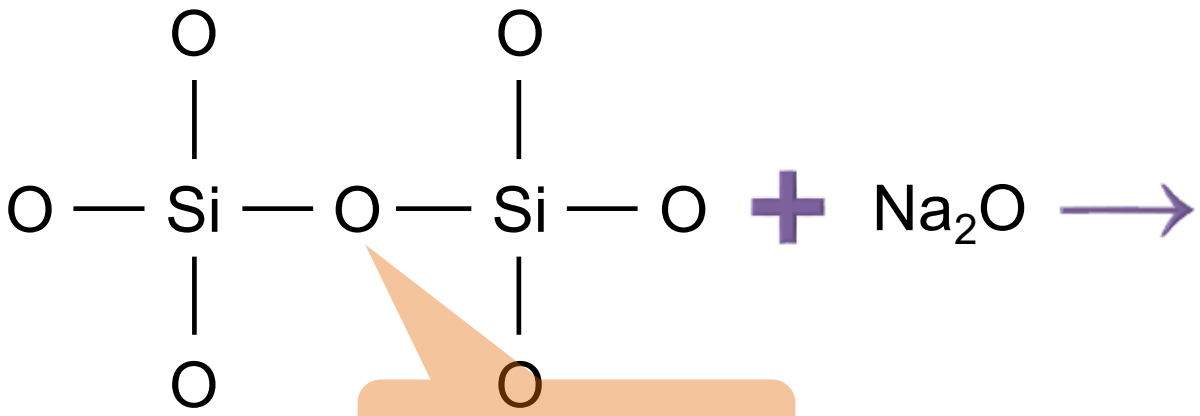
After-class reading list

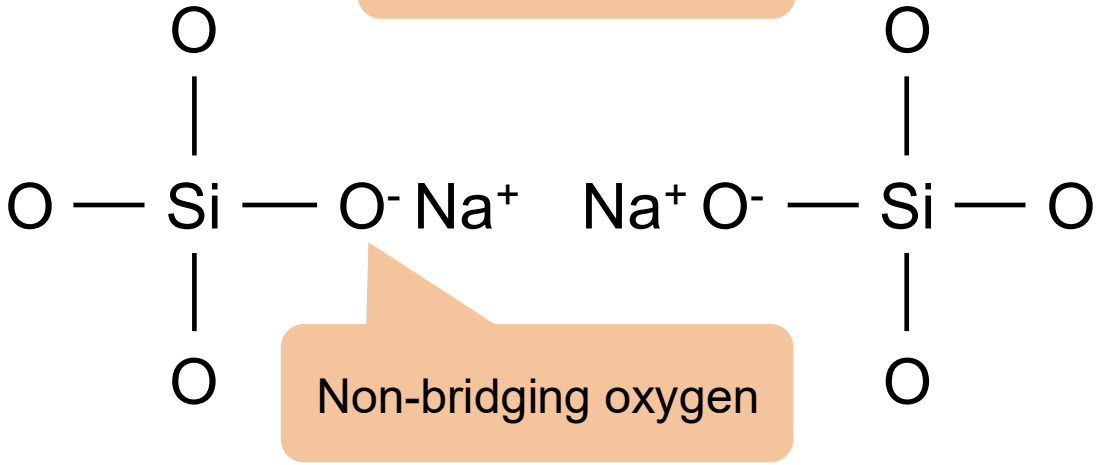
- Fundamentals of Inorganic Glasses
  - Ch. 1 & 5
- Introduction to Glass Science and Technology
  - Ch. 5

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

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

1 H Hydrogen 1.00794																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012182											5 B Boron 10.811	6 C Carbon 12.0107	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.9984032	10 Ne Neon 20.1797
11 Na Sodium 22.989770	12 Mg Magnesium 24.3050											13 Al Aluminum 26.981538	14 Si Silicon 28.0855	15 P Phosphorus 30.973761	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.955910	22 Ti Titanium 47.867	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938049	26 Fe Iron 55.845	27 Co Cobalt 58.933200	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.61	33 As Arsenic 74.92160	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium (98)	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.90550	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.710	51 Sb Antimony 121.760	52 Te Tellurium 127.60	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90545	56 Ba Barium 137.327	57 La Lanthanum 138.9055	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.078	79 Au Gold 196.96655	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98038	84 Po Polonium (209)	85 At Astatine (210)	86 Rn Radon (222)
87 Fr Francium (223)	88 Ra Radium (226)	89 Ac Actinium (227)	104 Rf Rutherfordium (261)	105 Db Dubnium (262)	106 Sg Seaborgium (263)	107 Bh Bohrium (262)	108 Hs Hassium (265)	109 Mt Meitnerium (266)	110 (269)	111 (272)	112 (277)	113	114				

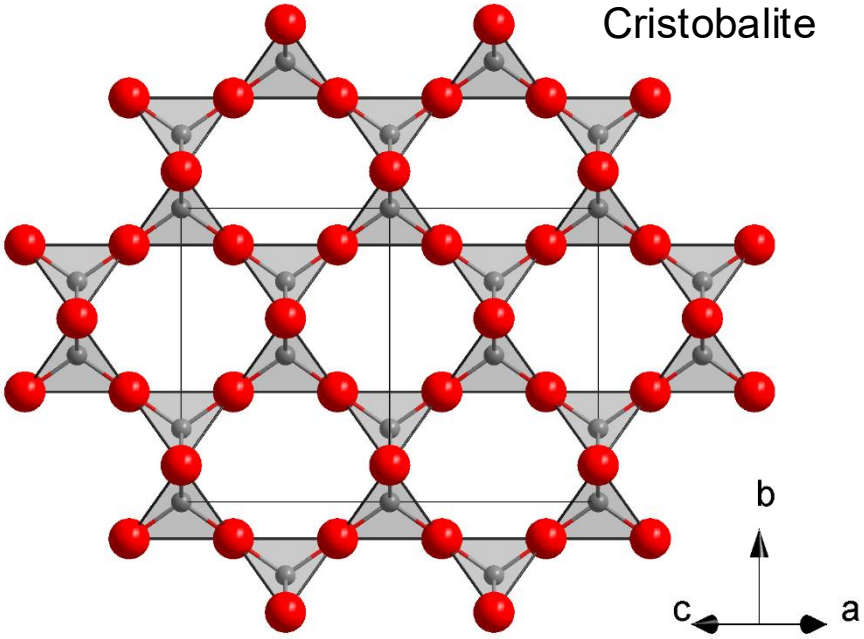
Network modifiers

Glass formers

Intermediates

Silica glass (SiO_2)

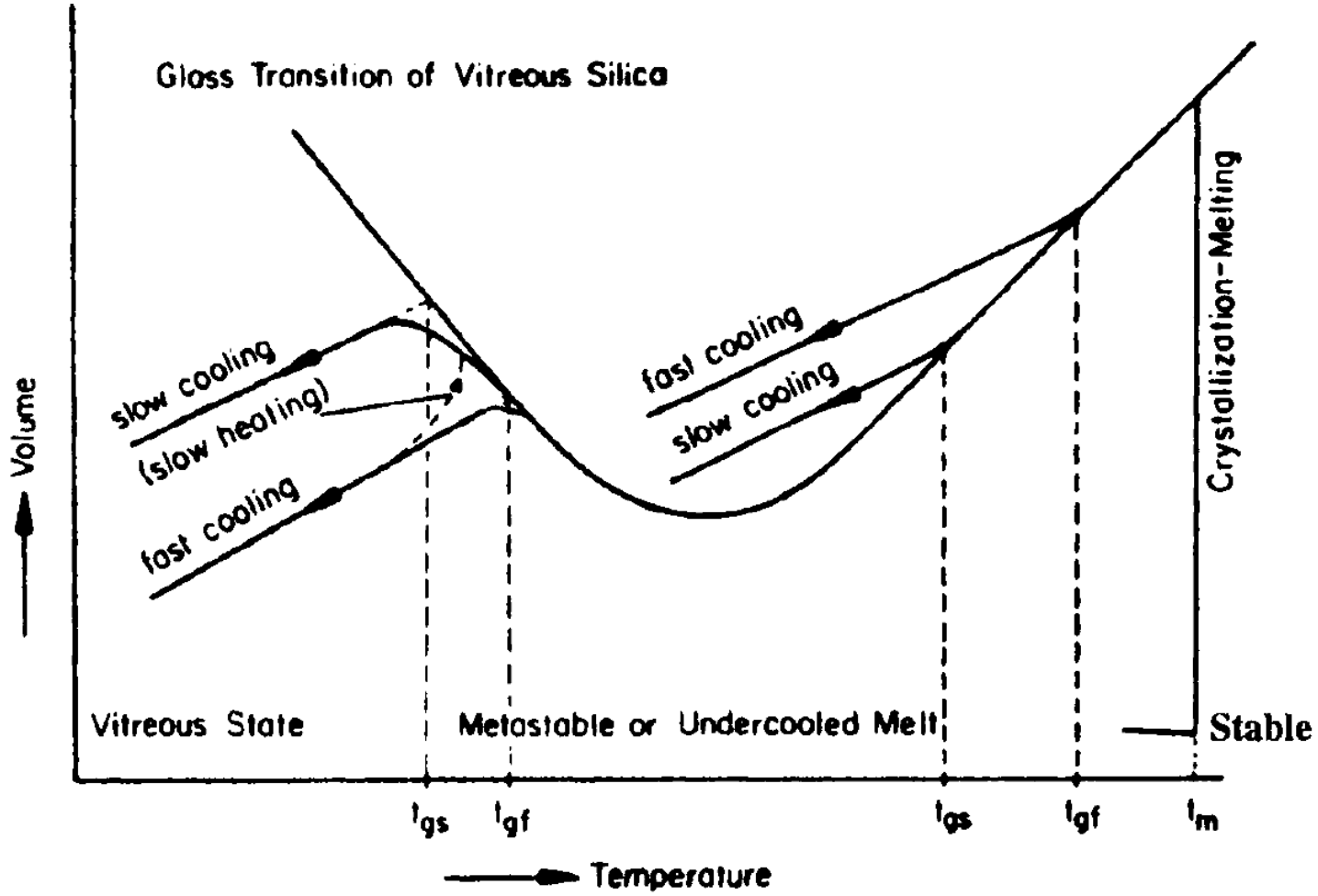
- A 3-D glass network predominantly consisting of corner-sharing SiO_4 tetrahedra interconnected by bridging oxygen (BO)
- High network connectivity: high softening point, low diffusion coefficient, small coefficient of thermal expansion (CTE)





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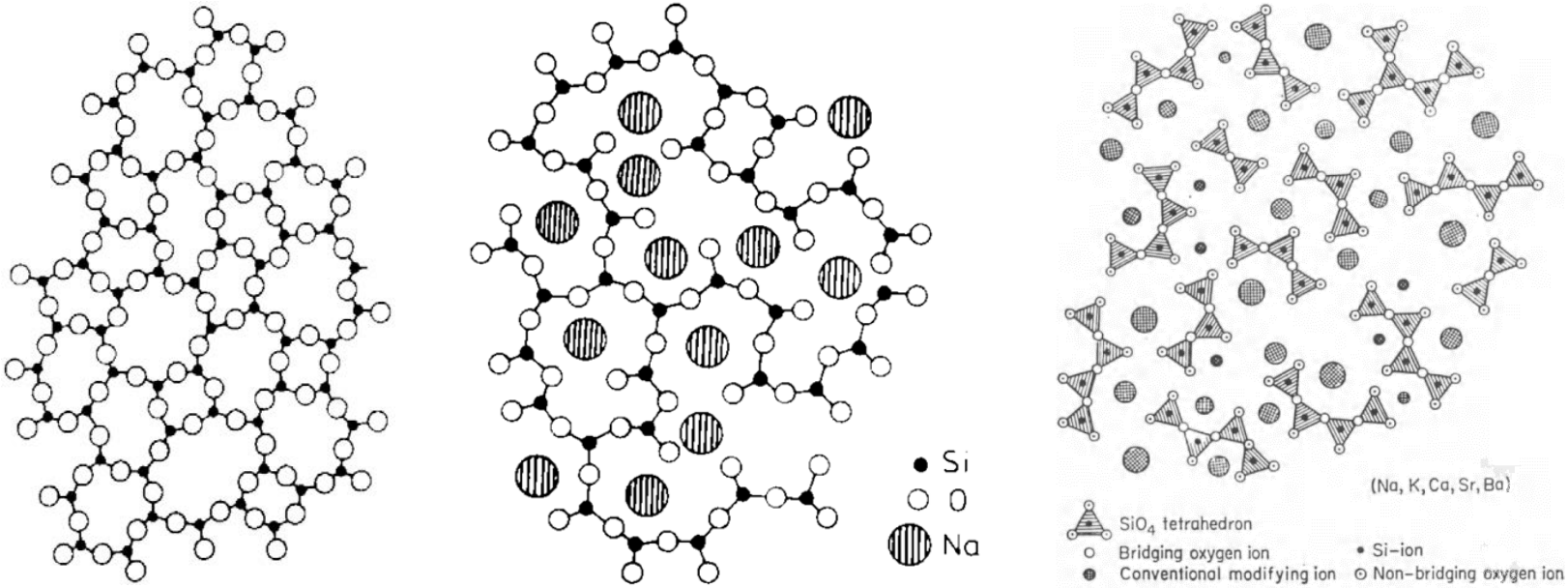
Volume anomaly in silica glass



R. Brückner, "Properties and structure of vitreous silica. I," *Journal of Non-Crystalline Solids*, Volume 5, Issue 2, 1970. https://www.sciencedirect.com. Used with permission.

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



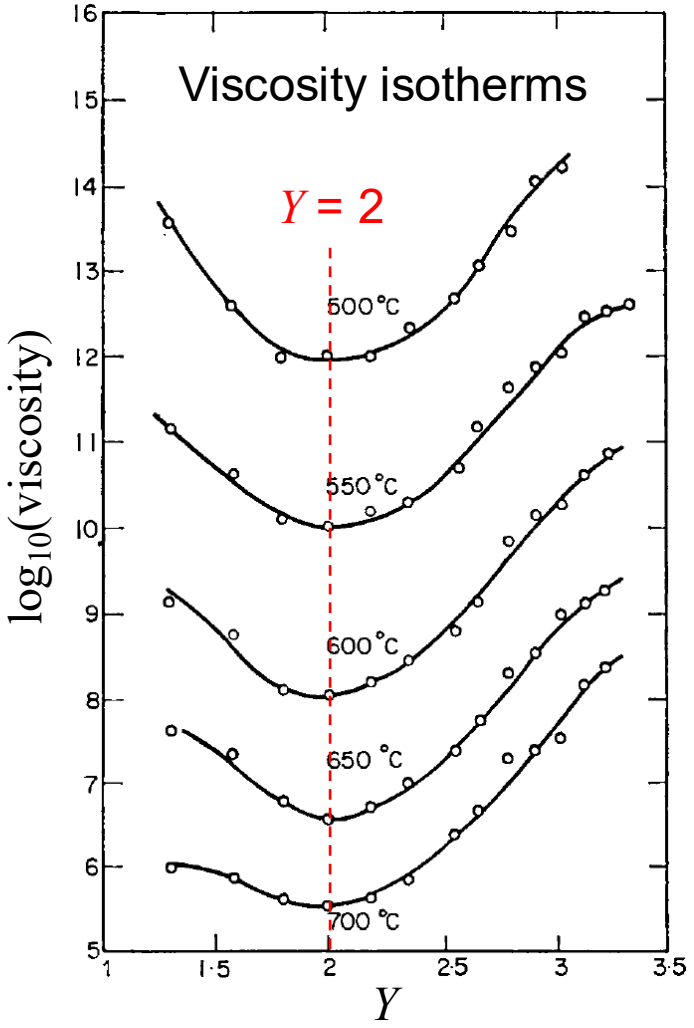
Invert glass

Source: public domain

Increasing alkali concentration

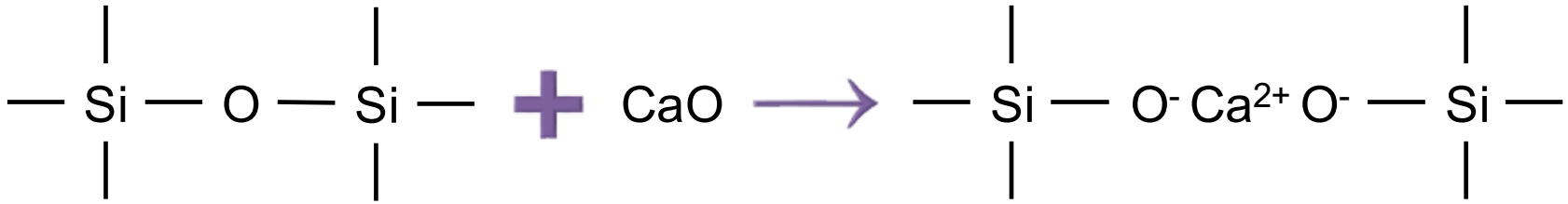
Structural determination in alkali silicate glass

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

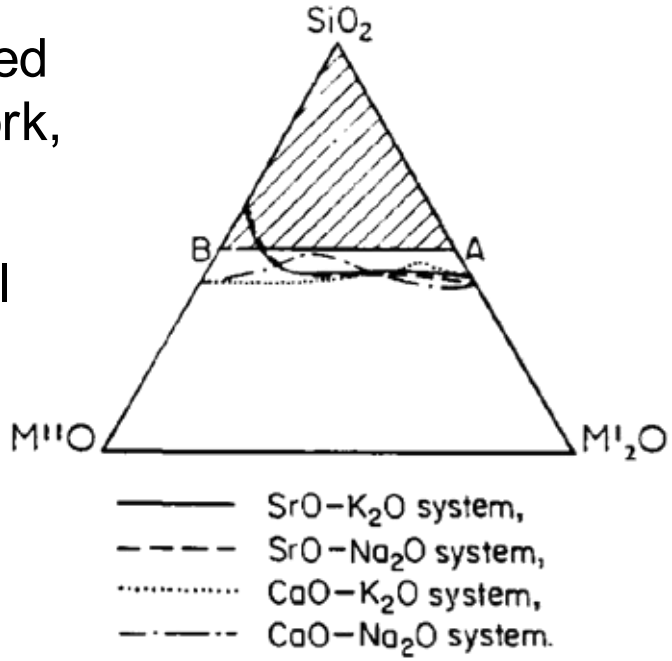


Alkali-alkaline earth-silicate glass

- Each alkaline earth ion creates two NBOs

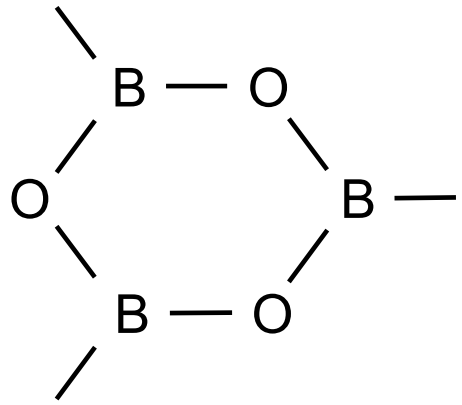


- Increased network connectivity compared to alkali silicates: stabilized glass network, improved chemical resistance
- Approximate composition of commercial soda-lime glass (window glass):
  - $16Na_2O \cdot 10CaO \cdot 74SiO_2$

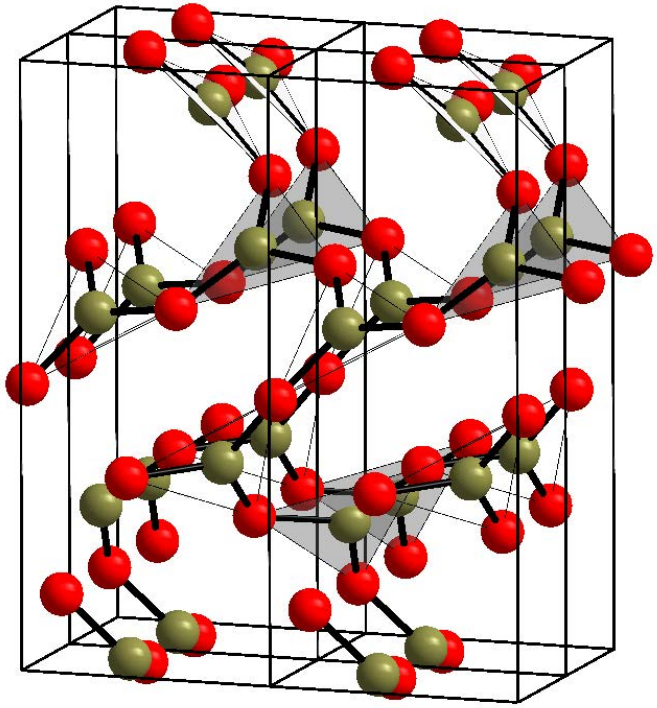


Borate glass

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



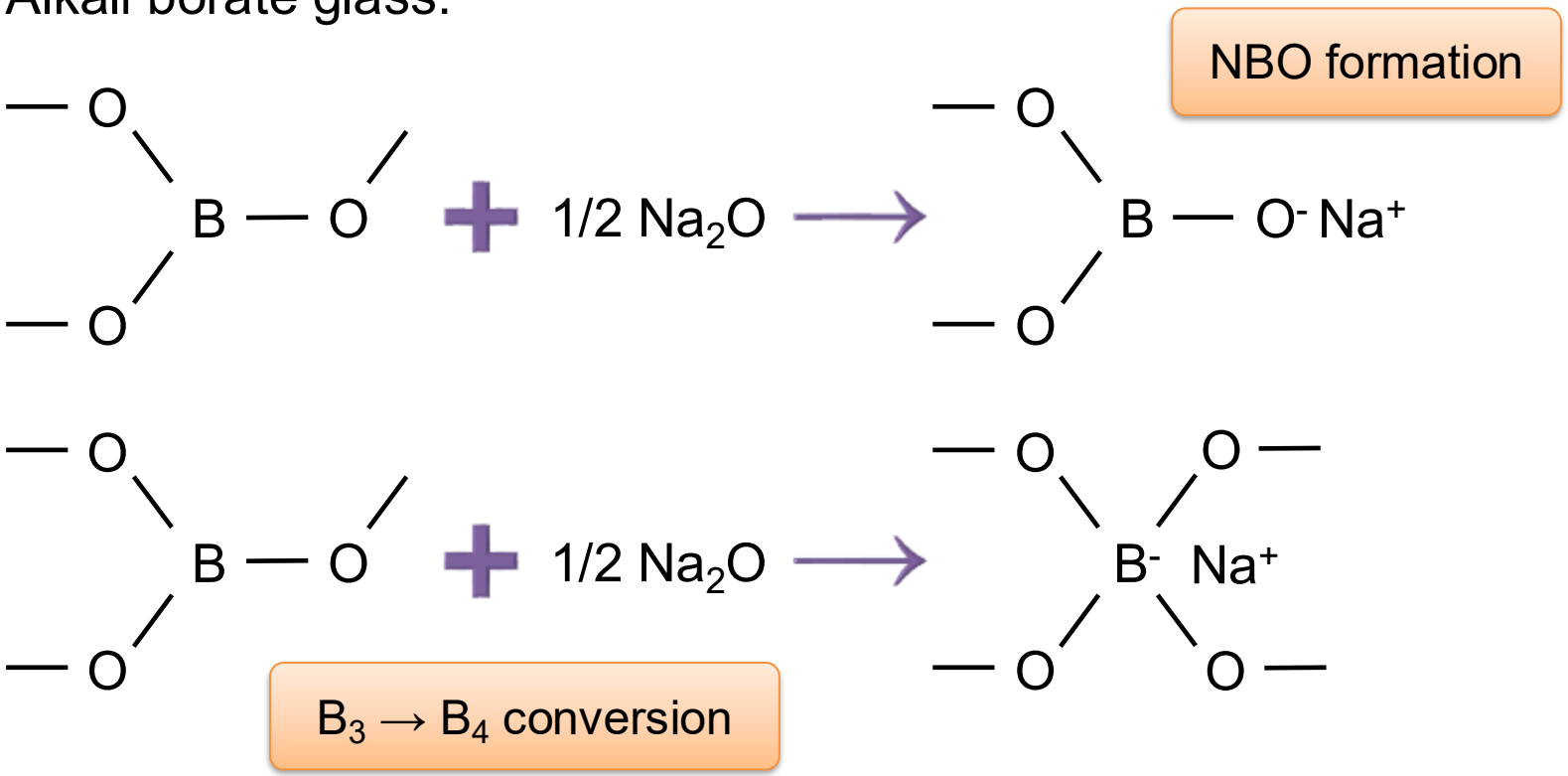
Boroxol rings: basic structural unit in boric oxide glass



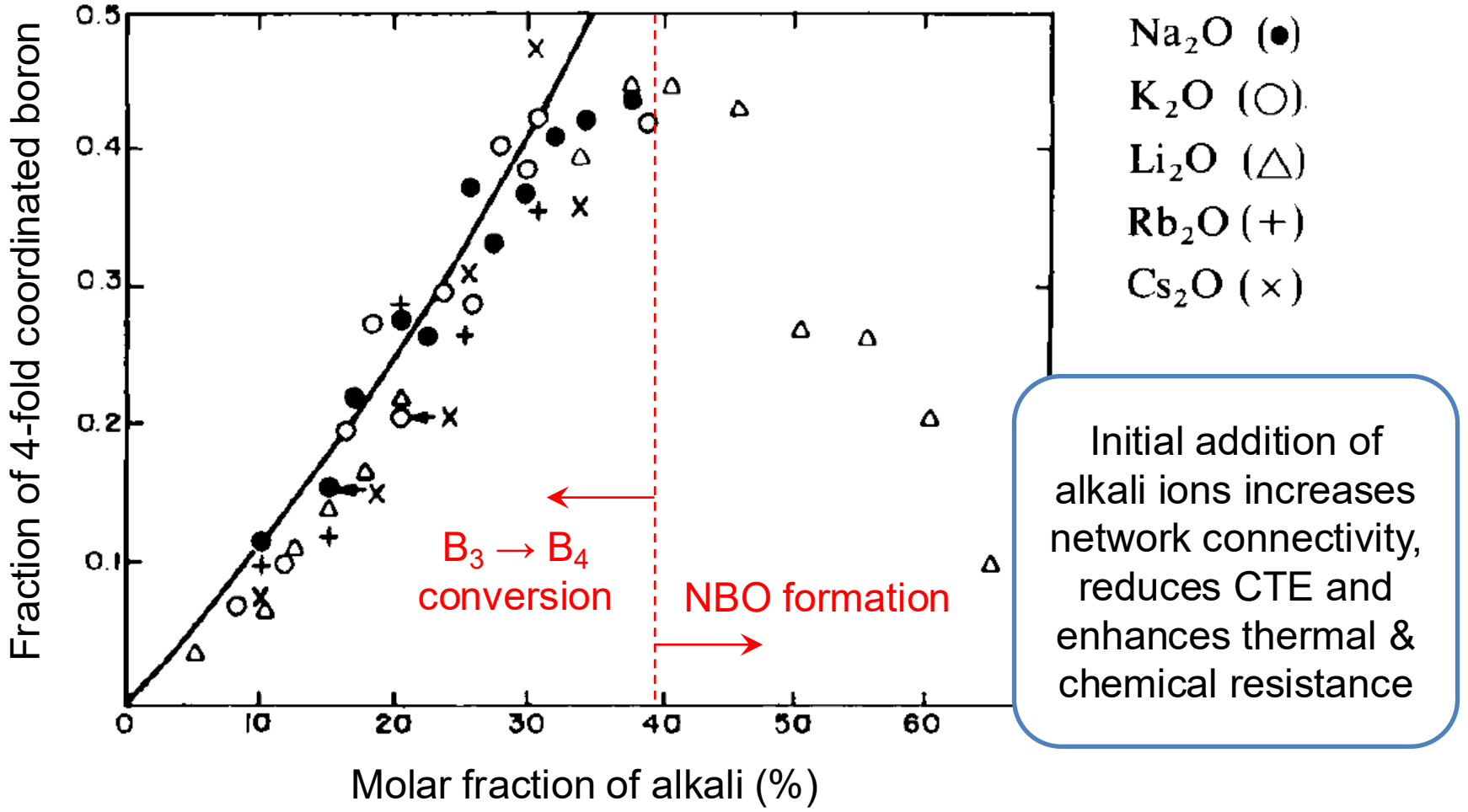
B_2O_3 crystal

Borate glass

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

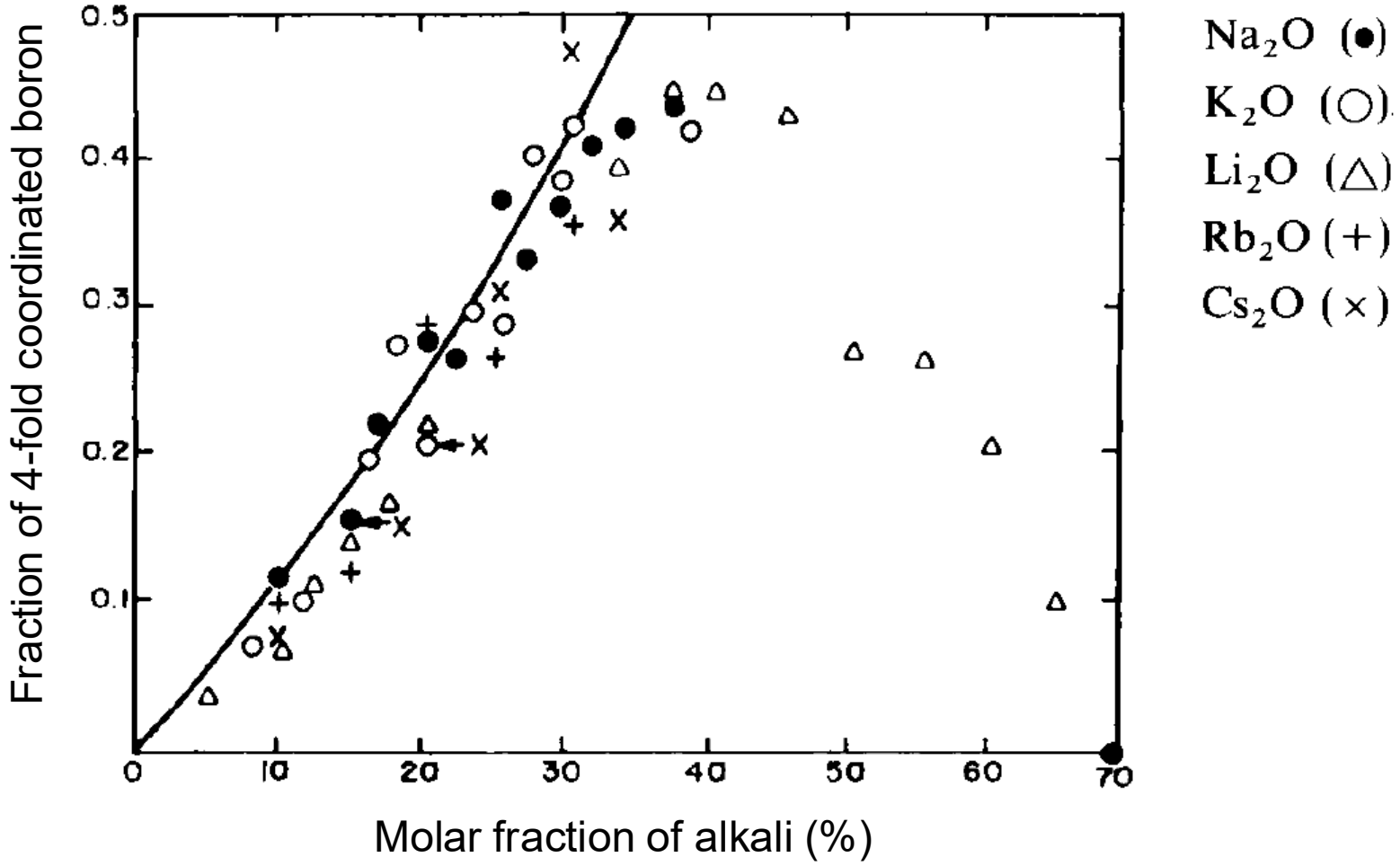


The Boron anomaly



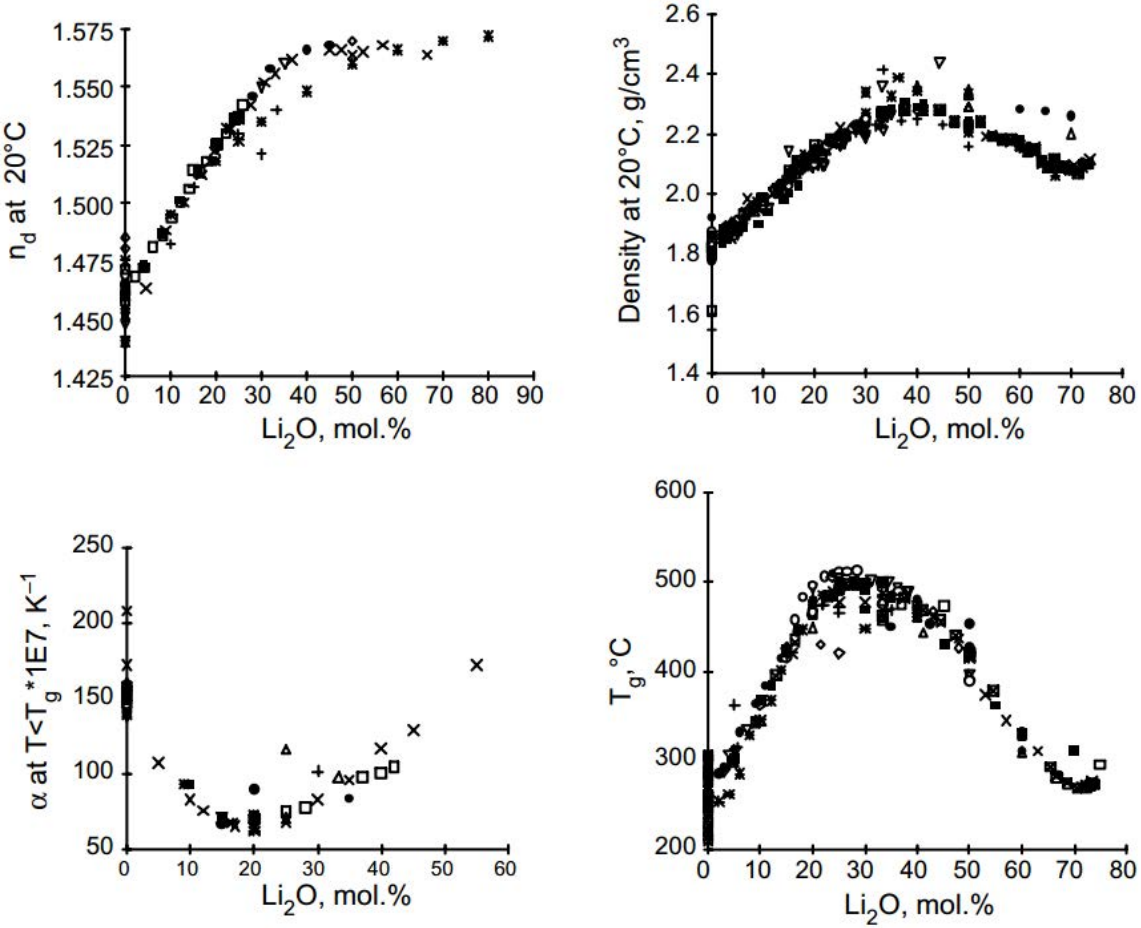
Initial addition of alkali ions increases network connectivity, reduces CTE and enhances thermal & chemical resistance

The Boron anomaly



O.V. Mazurin, "Glass properties: compilation, evaluation, and prediction," Journal of Non-Crystalline Solids, Volume 351, Issues 12–13, 2005, Pages 1103-1112. https://www.sciencedirect.com. Used with permission.

Various properties of lithium borate glass



More than two structural transformations contribute to the boron anomaly

Further reading: Shelby Ch. 5

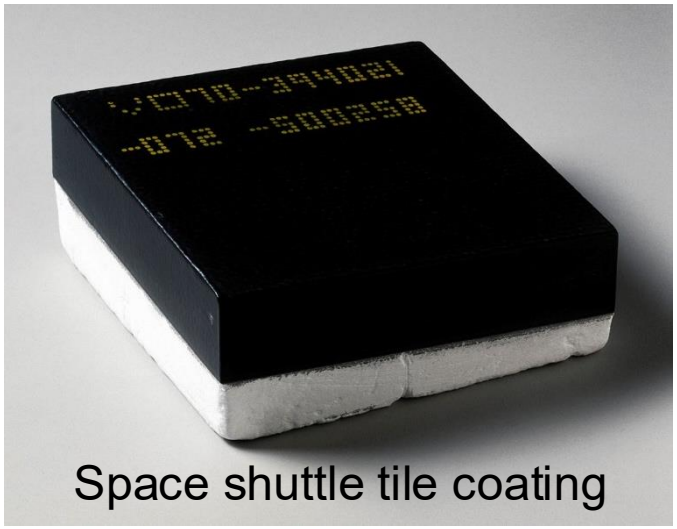
J. Non-Cryst. Sol. **351**, 1103-1112 (2005)

O.V. Mazurin, "Glass properties: compilation, evaluation, and prediction," Journal of Non-Crystalline Solids, Volume 351, Issues 12–13, 2005, Pages 1103-1112. https://www.sciencedirect.com. Used with permission.

(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: $4Na_2O{\cdot}13B_2O_3{\cdot}2Al_2O_3{\cdot}81SiO_2$



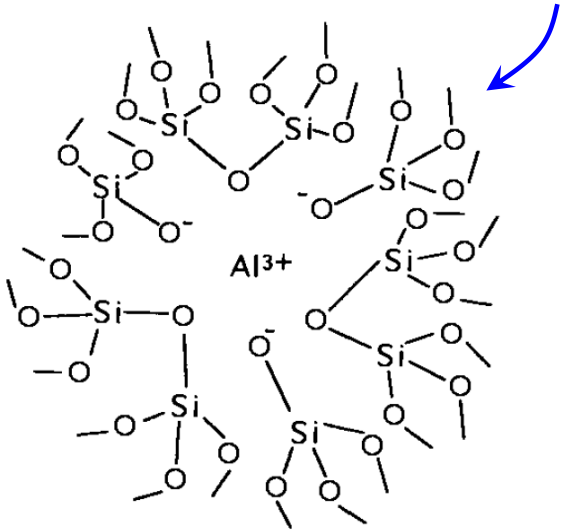

Space shuttle tile coating



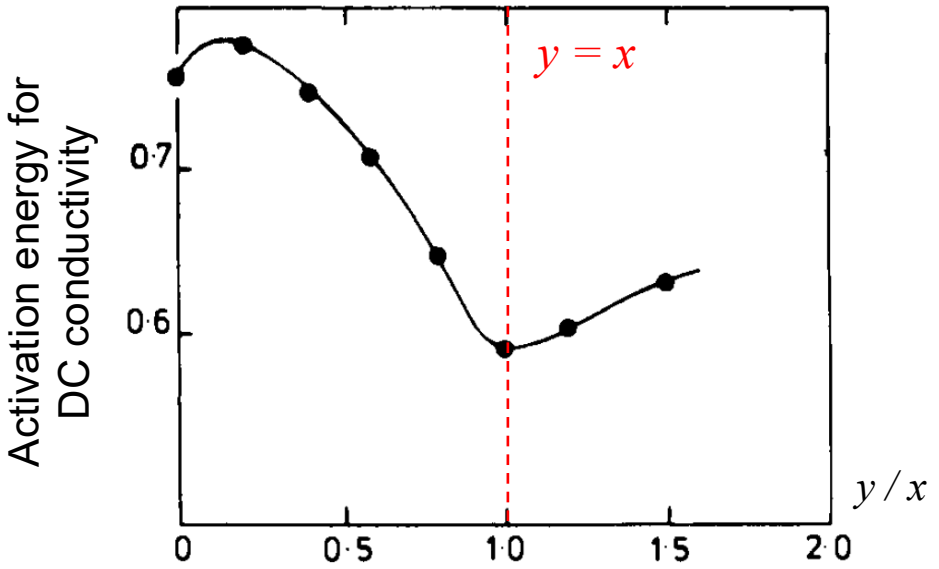
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(Alkali) aluminosilicate glass

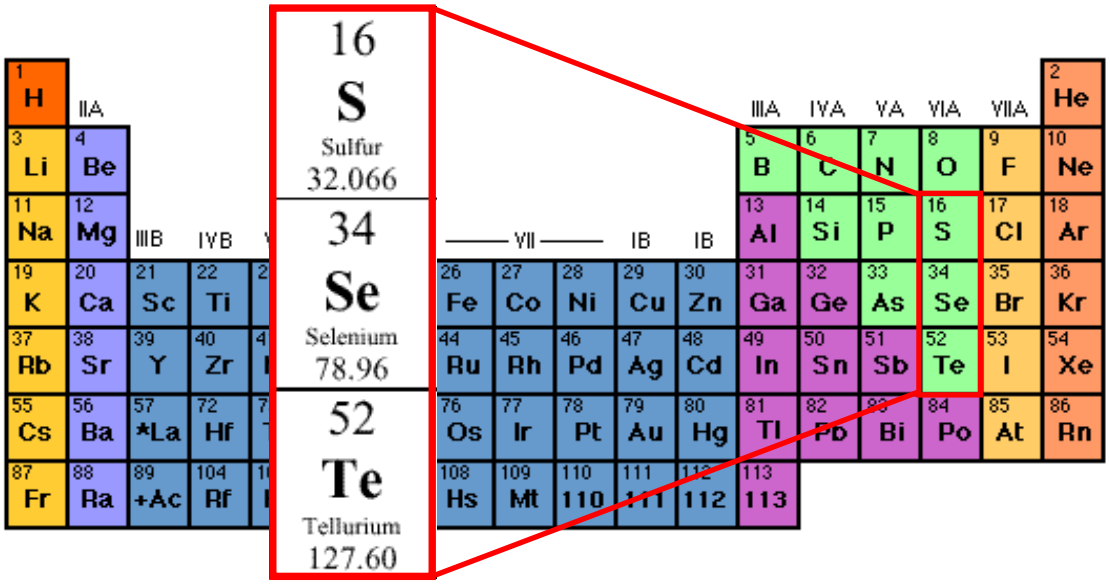
- Aluminosilicate glass: $x\ M_2O \cdot y\ Al_2O_3 \cdot (1 - x - y)\ SiO_2$
  - SiO_2 : glass former
  - Al functions as a glass former in the form of AlO_4 groups (when $x > y$)
  - Each excess Al atom creates three NBOs (when $x < y$)



Al^{3+} in an oxygen octahedron



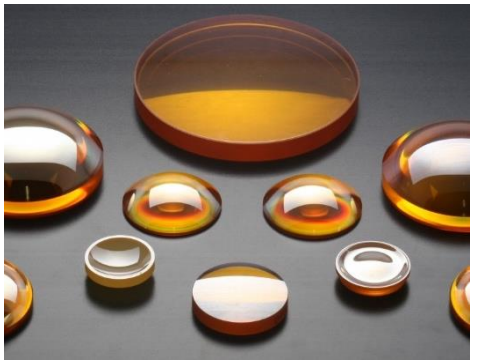
Chalcogenide glass (ChG)





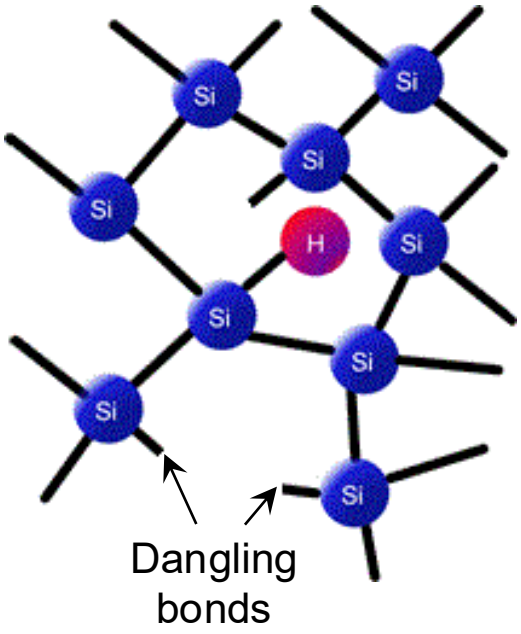
ACerS Bull. **94**, 24-29 (2015)

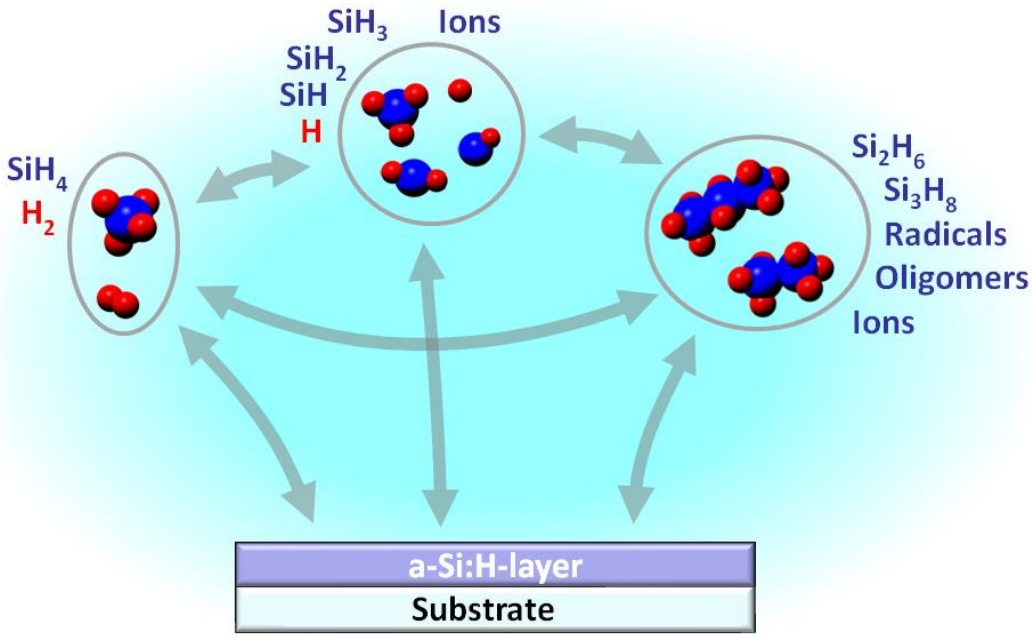
- Reduced mechanical strength
- Low softening temperature
- Low phonon energy (infrared transparency)
- Enhanced optical (Kerr) nonlinearity



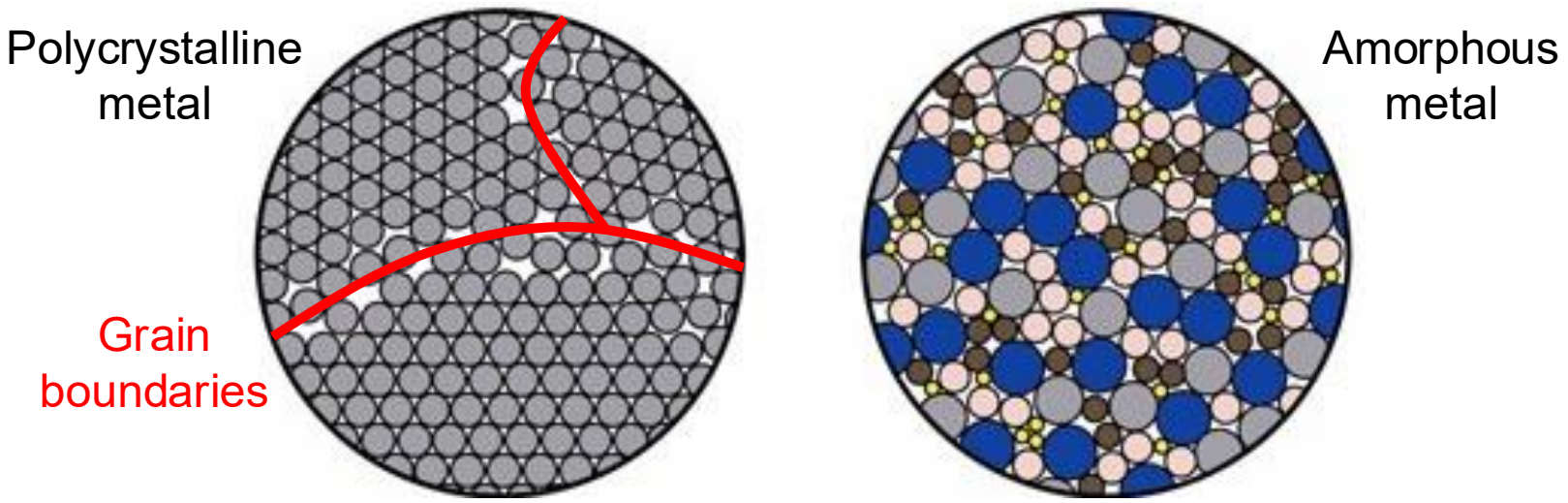
Amorphous semiconductors

- 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)



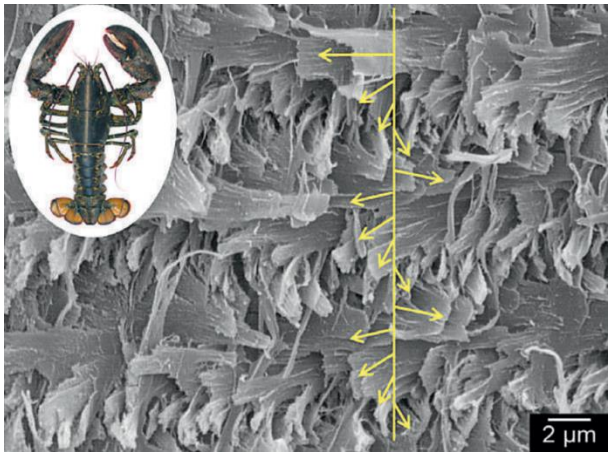
- Inoue's empirical rules for bulk metallic glass (BMG) formation
  - Multicomponent systems consisting of three or more elements
  - Significant difference in atomic size ratios (frustration)
  - Negative enthalpy of mixing

© Risch, Nicholas & Schauer, Jan & Shah, Naimish & Pede, Dennis & Luzius, Severin & Fu, Eliana. (2023). "Unique materials for additive manufacturing enabling new series application," at SPIE Laser 3D Manufacturing X. All rights reserved. This content is excluded from our Creative Commons license. For more information, see https://ocw.mit.edu/help/faq-fair-use/

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/amorphous systems
  - Chalcogenides: weak bonds
  - Group IV amorphous semiconductors: 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

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