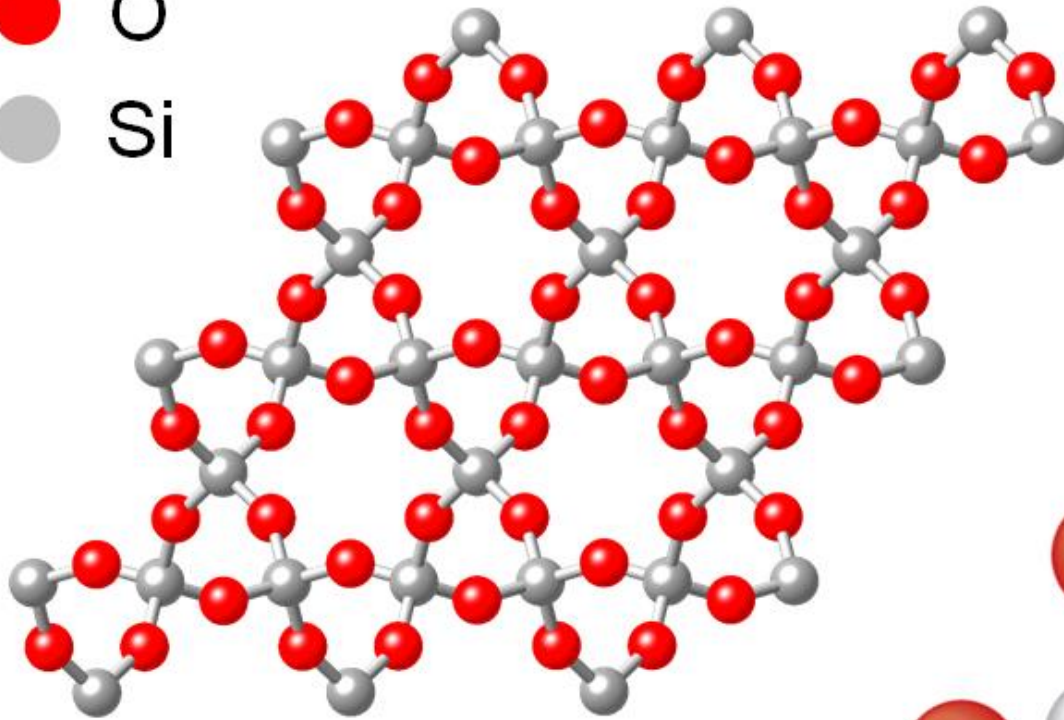


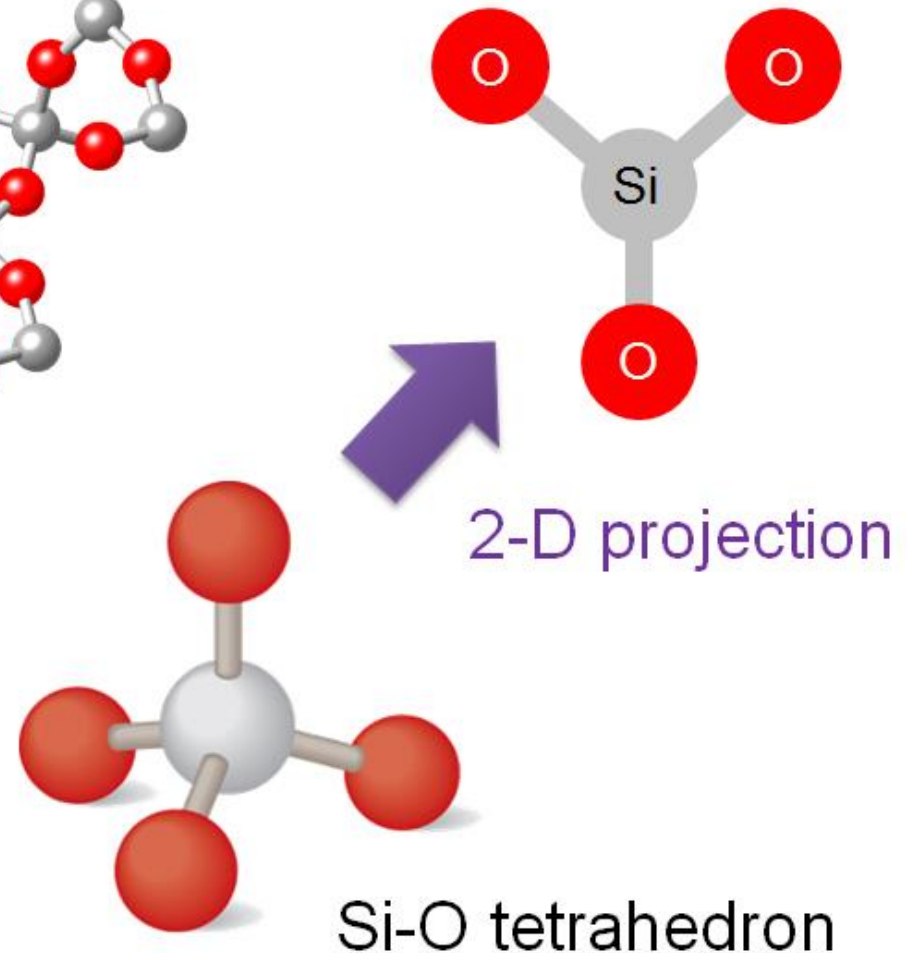
MATERIAIS CERÂMICOS E VIDROS

GLASS STRUCTURE

Direct atomic imaging of bilayer silica glass

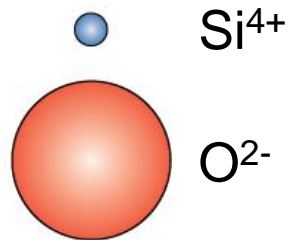
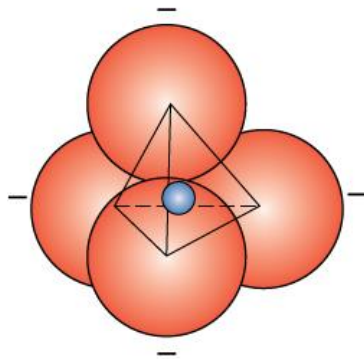


Quartz crystal

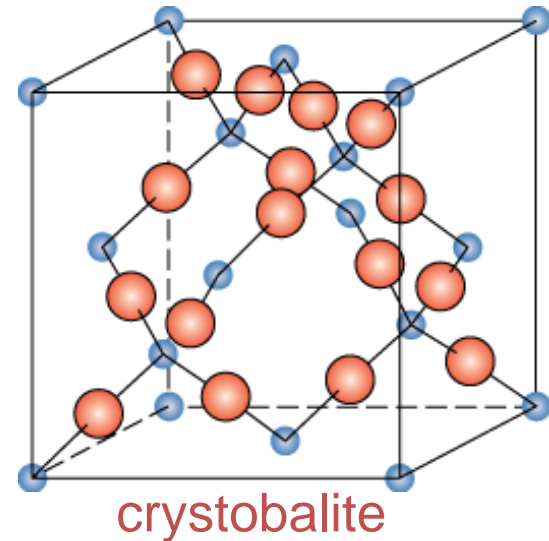


Silica (Glass)

- In quartz, the O-Si-O angle is $109^{\circ}28'$ and the Si-O-Si angles are $\sim 150^{\circ}$.

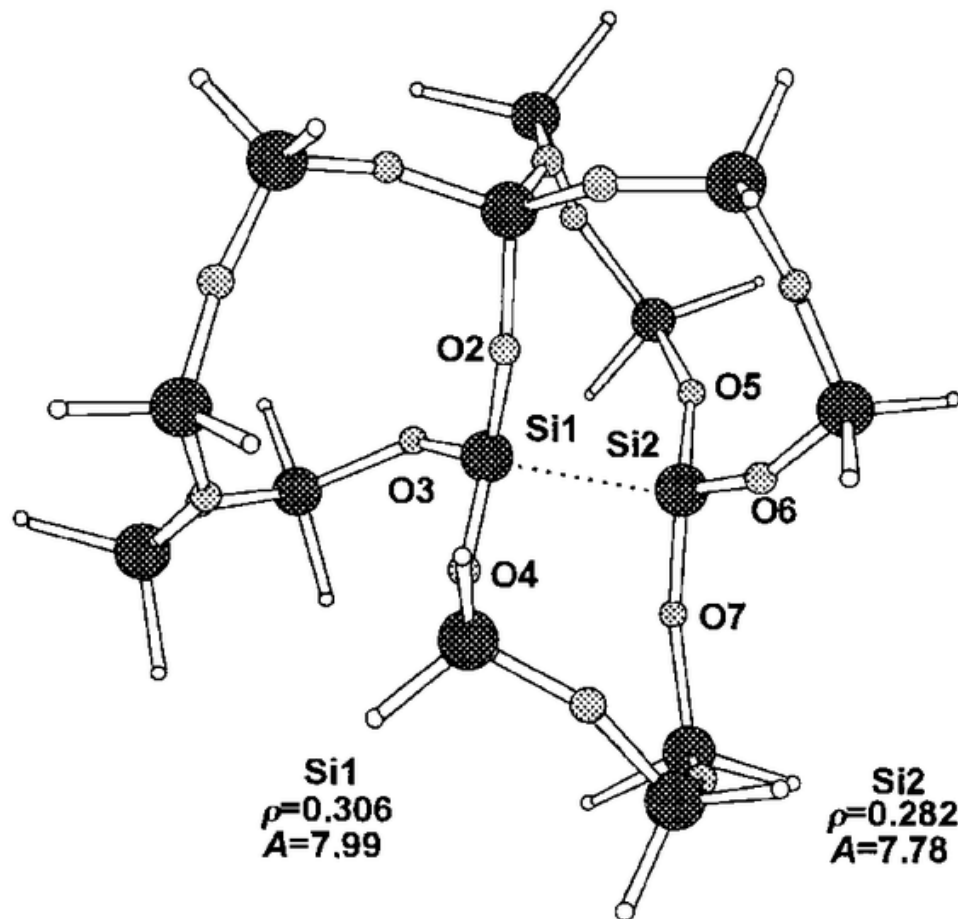


Adapted from Figs.
12.9-10, *Callister 7e*.



- In amorphous silica, they are $109^{\circ}28'$ and a large distribution between 110° and 180° .

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



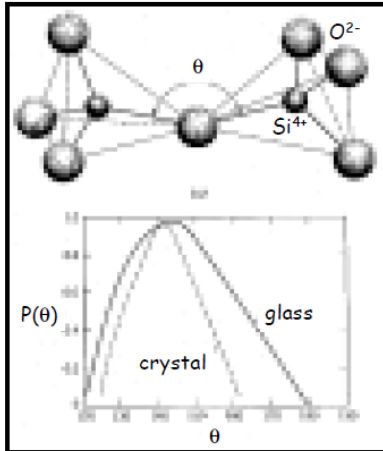
Bond distances (Å)

Si1–O2=1.605
Si1–O3=1.610
Si1–O4=1.607
Si2–O5=1.603
Si2–O6=1.604
Si2–O7=1.606
Si1–Si2=2.557

Bond angles (degree)

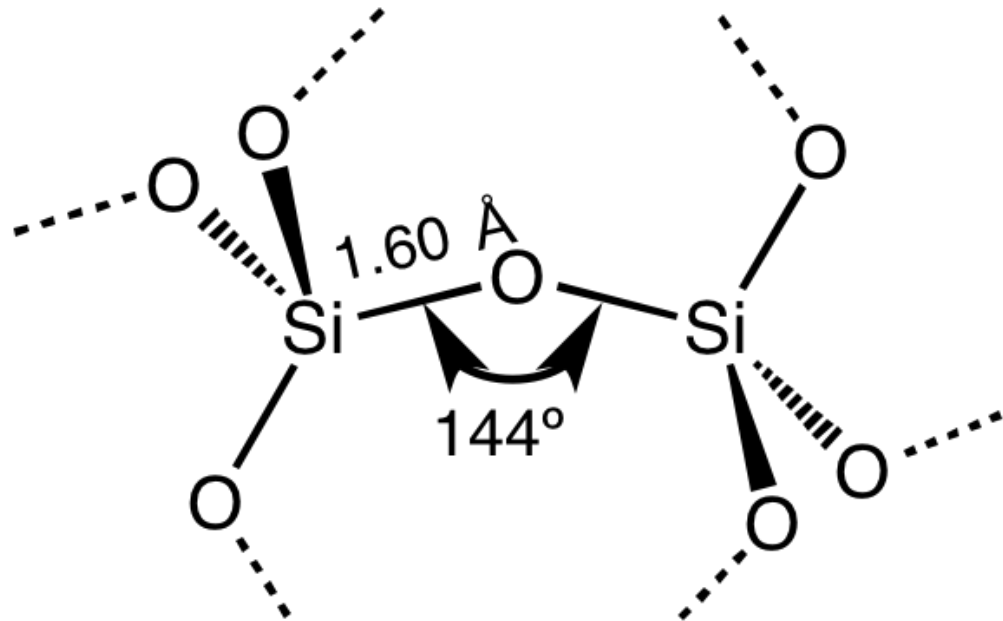
O2–Si1–O3=116.4
O2–Si1–O4=115.4
O3–Si1–O4=114.9
O5–Si2–O6=115.6
O5–Si2–O7=115.0
O6–Si2–O7=115.0

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.

**Short range order ~20 Å,
~ 3 - 4 coordination
polyhedra!**



Glass consists of a continuous atomic network

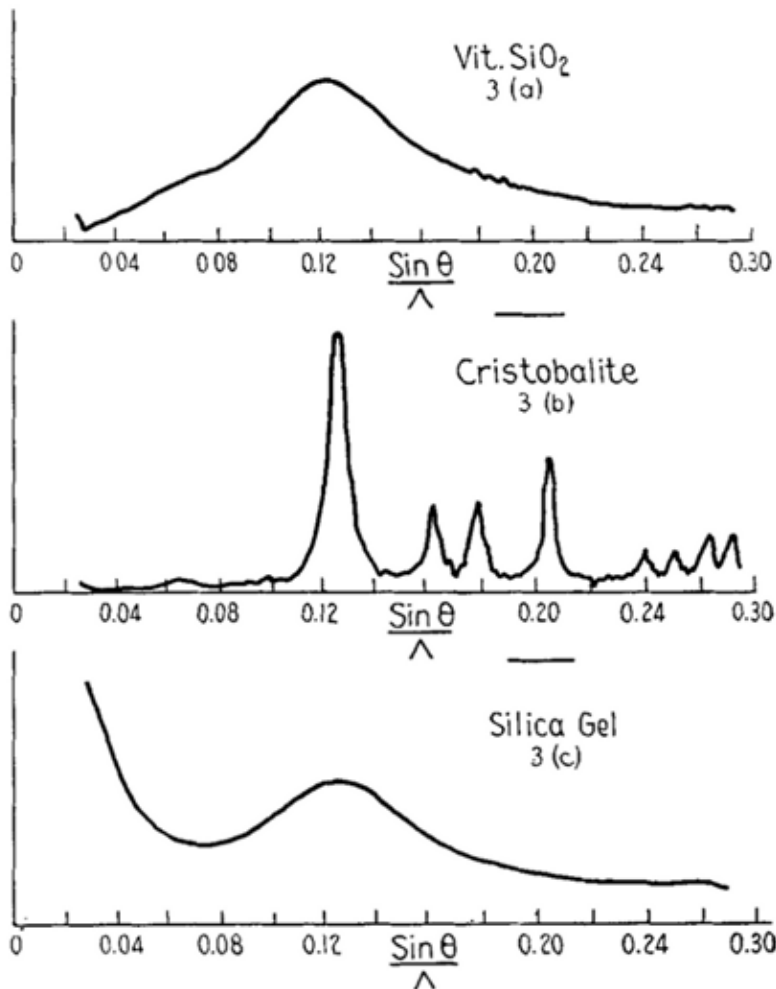


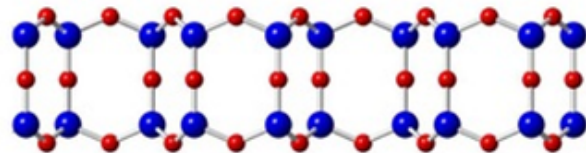
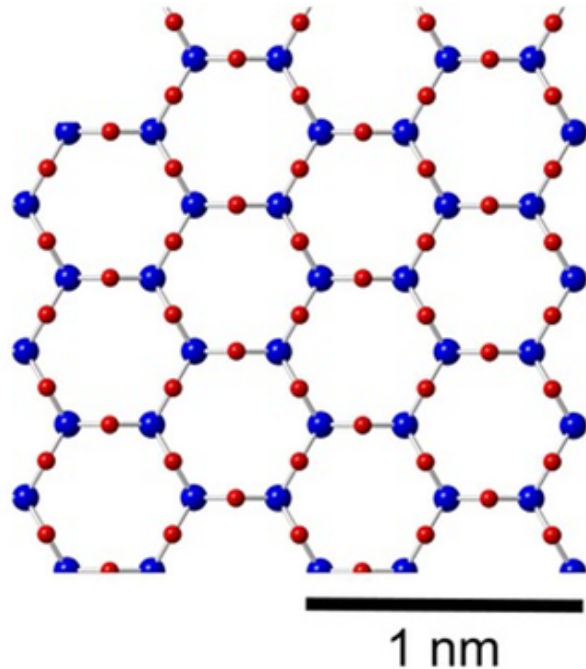
FIG. 3.—Microphotometer records of X-ray diffraction patterns; (a) vitreous silica, (b) cristobalite, and (c) dried commercial silica gel.

- Absence of small angle scattering
 - Continuous structure without micro-voids
- Broad diffraction peak
 - Size of ordered region $< 8 \text{ \AA}$ (Scherrer equation)
 - Unit cell size of cristobalite: 7.1 \AA

Glass is NOT a collection of extremely small crystals

J. Am. Cer. Soc. **21**, 49-54 (1938).

Direct atomic imaging of bilayer silica glass



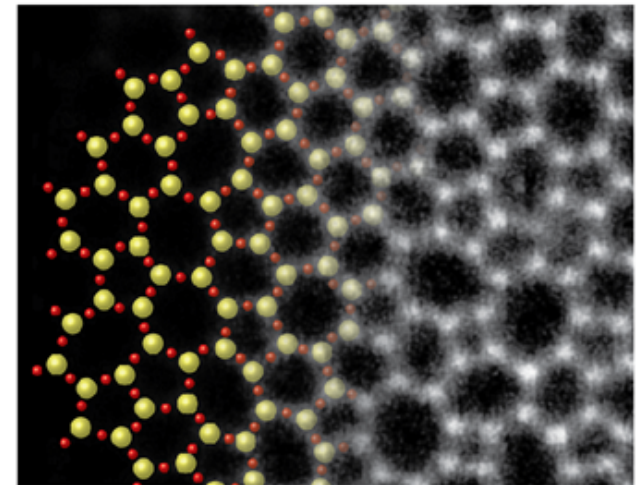
Sci. Rep. **3**, 3482 (2013).

Sept. 12, 2013

Shattering records: Thinnest glass in Guinness book

By *Anne Ju*

At just a molecule thick, it's a new record: The world's thinnest sheet of glass, a serendipitous discovery by scientists at Cornell and Germany's University of Ulm, is recorded for posterity in the Guinness Book of World Records.



STEM images of 2-D silica crystal and glass

Nano Lett. **12**, 1081-1086 (2012).

STRUCTURE OF GLASSES

Zachariasen observed similar mechanical properties (elastic modulus, ...) between glasses and crystals. So **similar structural energies** between (chemically identical) **crystals** and **glasses** were expected!

Identical atomistic building blocks (cation polyhedra) are expected.

However, glasses have **greater structural energies**!

Glasses **lack the periodic (long range)** order of a crystal

Glasses exhibited **infinite unit cell** (no repeating large scale properties)

Glasses show **3D network lacking symmetry and periodicity**

Glasses are **ISOTROPIC**: same average packing and properties in all directions

STRUCTURE OF GLASSES

Zachariasen recognized that **crystal chemistry rules and patterns also apply to glasses**. Certain polyhedra are more likely to form the disorder 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?**

... remember the Pauling rules...

First rule: the radius ratio rule

A coordinated polyhedron of anions is formed about each cation, the cation-anion distance equaling the sum of their characteristic packing radii and the **coordination polyhedron being determined by the radius ratio.**

Second rule: the electrostatic valence rule

An ionic structure will be stable to the extent that **the sum of the strengths of the electrostatic bonds that reach an anion equal the charge on that anion.**

Third rule: sharing of polyhedron corners, edges and faces

The **sharing of edges and particularly faces** by two anion polyhedra **decreases the stability of an ionic structure.**

Fourth rule: crystals containing different cations

In a crystal containing different cations, those of **high valency and small coordination number tend not to share polyhedron elements with one another.**

Fifth rule: the rule of parsimony

The number of essentially different kinds of constituents in a crystal tends to be small.

STRUCTURE OF GLASSES

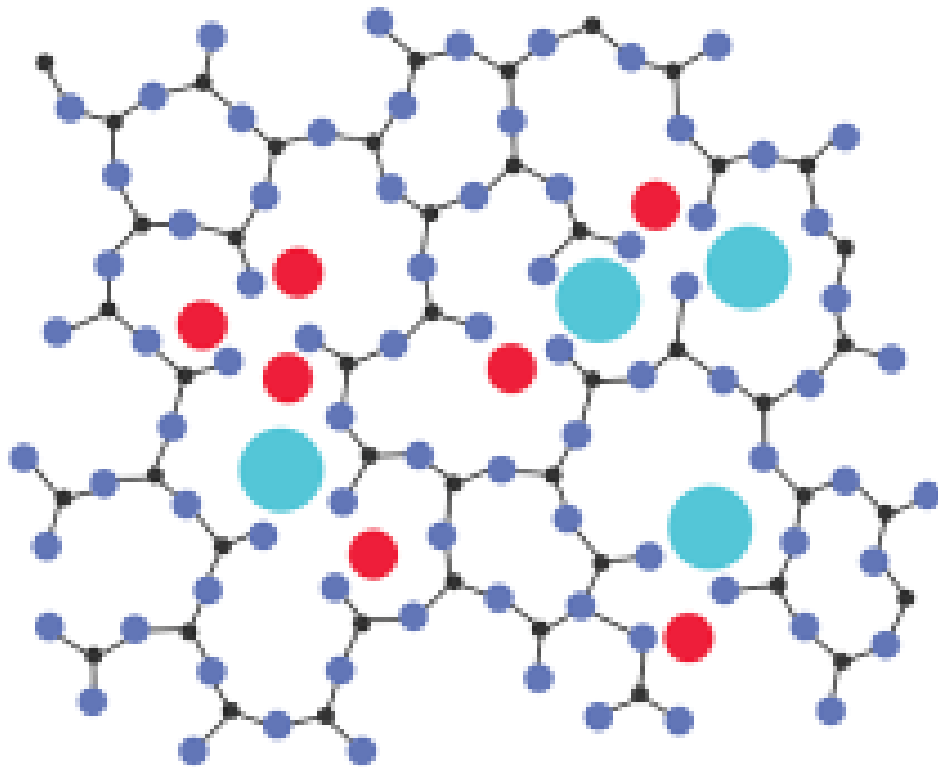
Zachariasen's Rules for Glass Formation: (empirical observations for oxides)

1. No oxygen atom may be linked to more than two cations
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.

STRUCTURE OF GLASSES



In glasses:

More is more!

(see kinetic model...)



In crystals:

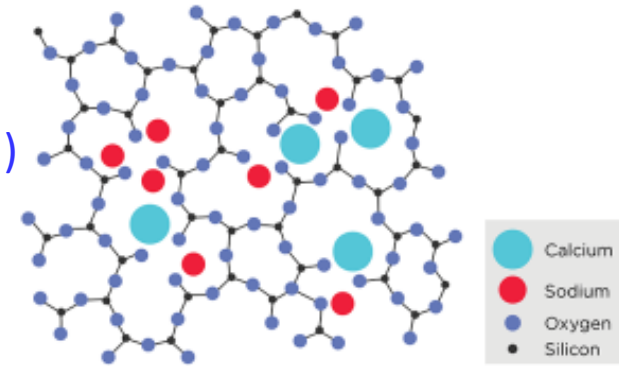
Pauling Fifth rule: the rule of parsimony

The number of essentially different kinds of constituents in a crystal tends to be small.

Less is more!

STRUCTURE OF GLASSES

Network former – allows an ease glass formation (even alone!)



Glass modifier - provides extra oxygen ions to the structure but does not participate in the network, thereby raising the O/Si ratio of the glass.

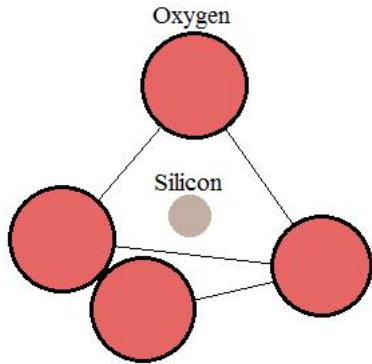
The extra oxygen atoms (apported by the modifier) disrupt the siloxane bonds $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ and form two new non-bridging oxygens ($\equiv\text{Si}-\text{O}_{\text{nb}}\cdots\cdots\text{nb}\text{O}-\text{Si}\equiv$) to terminate each tetrahedra.

Glass intermediate – is not clearly modifier or network former and may contribute in part to the network structure. They are generally cations with higher valence than the alkalis and alkaline earths, but which do not satisfy Zachariasen's rules.

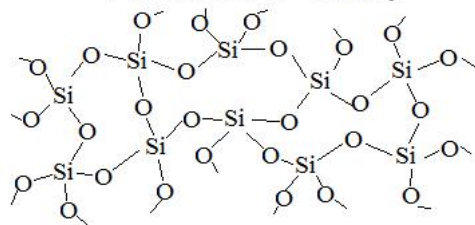
GLASS former

STRUCTURE OF GLASSES

Single SiO_4 Tetrahedron

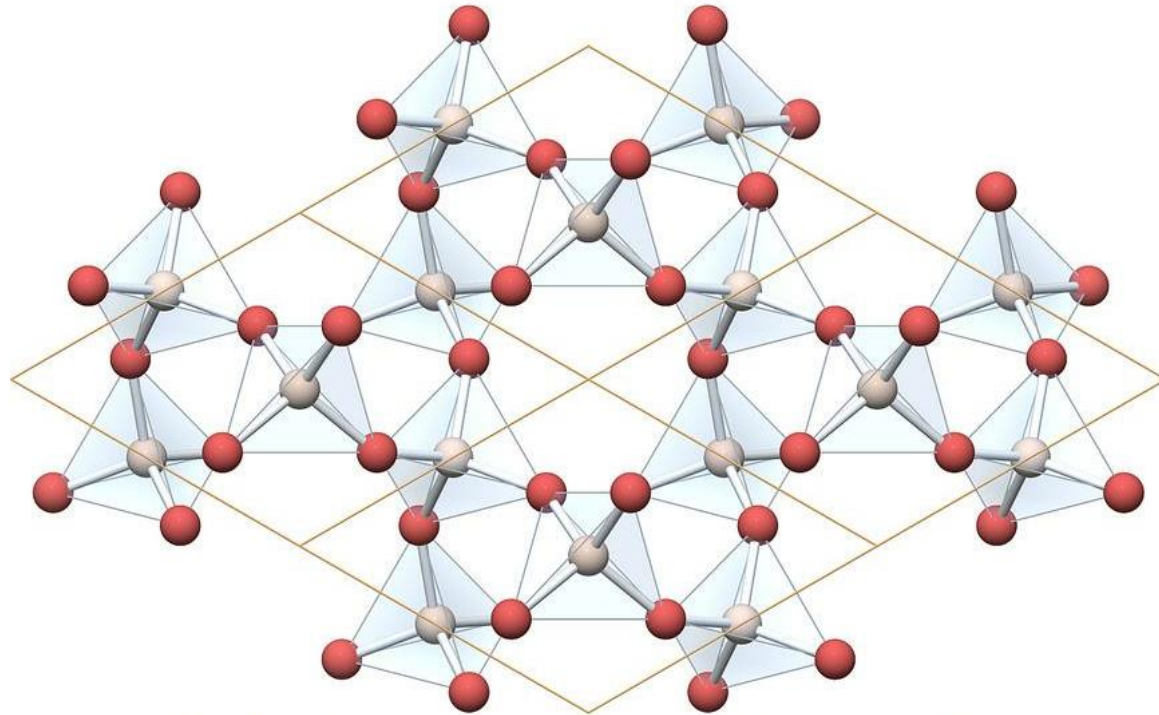


Distorted 2-D "Reality"



Notice: every silicon atom has exactly 4 oxygen bonds, and every oxygen atom has exactly 2 silicon bonds

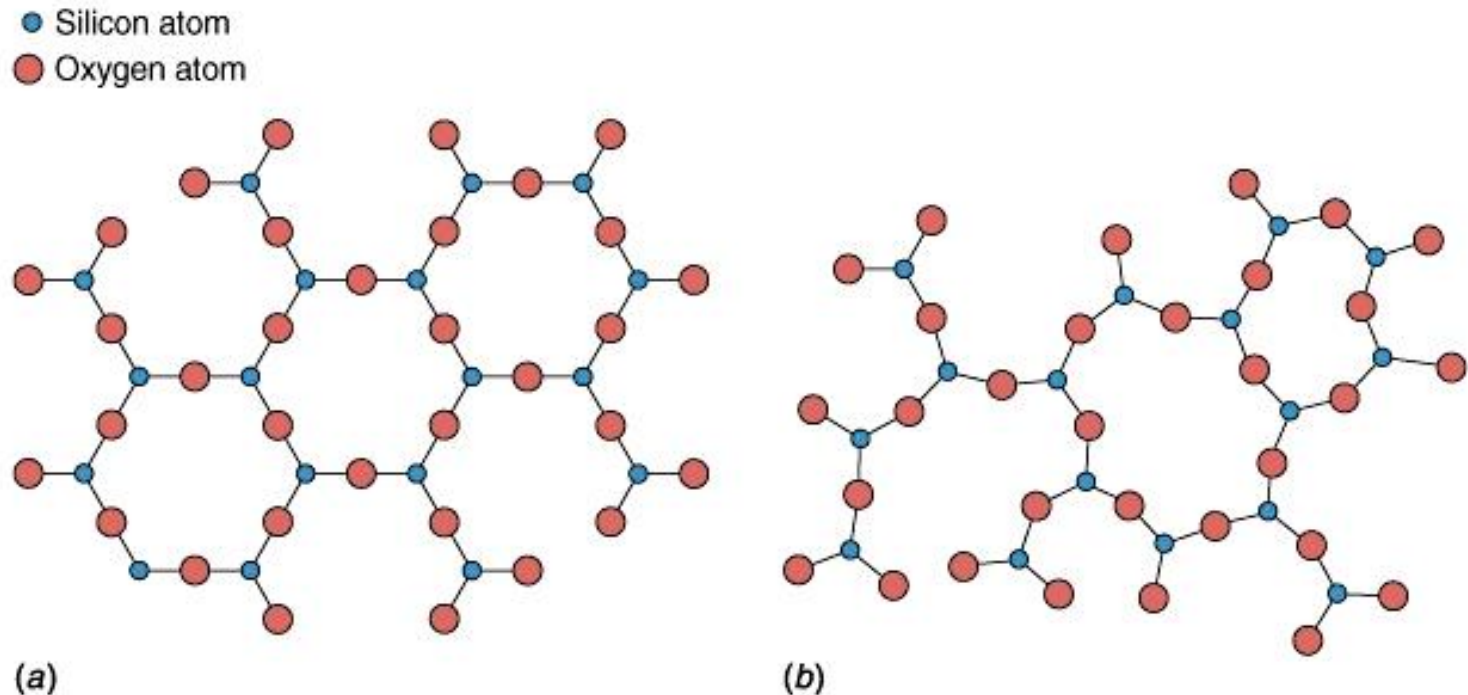
SiO_4 network



Notice: the tetrahedra join at the oxygen corners. Also, this structure is actually too uniform to be amorphous silica. This is more like crystalline silica (cristobalite)
Source: http://www.quartzpage.de/cr/gen_struct_fig1013_scl.jpg

GLASS former

STRUCTURE OF GLASSES



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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

GLASS former

1. Consider Silica:

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

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

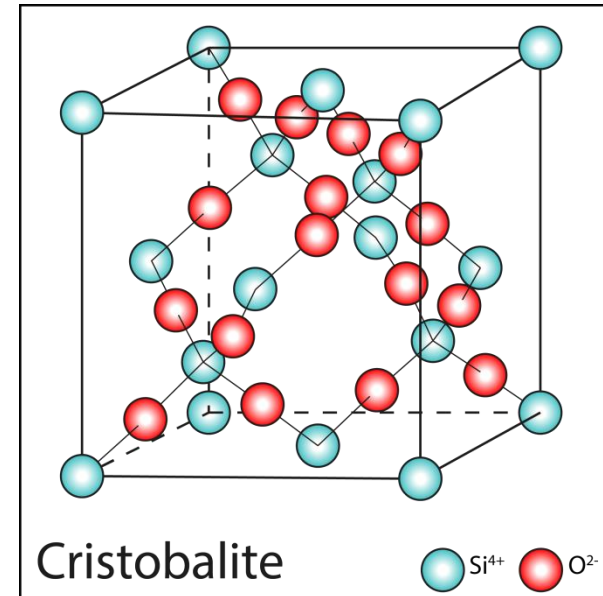
- satisfies Zachariasen's rule #2.

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

- satisfies Zachariasen's rule #1.

Crystal structure: sharing four corners:

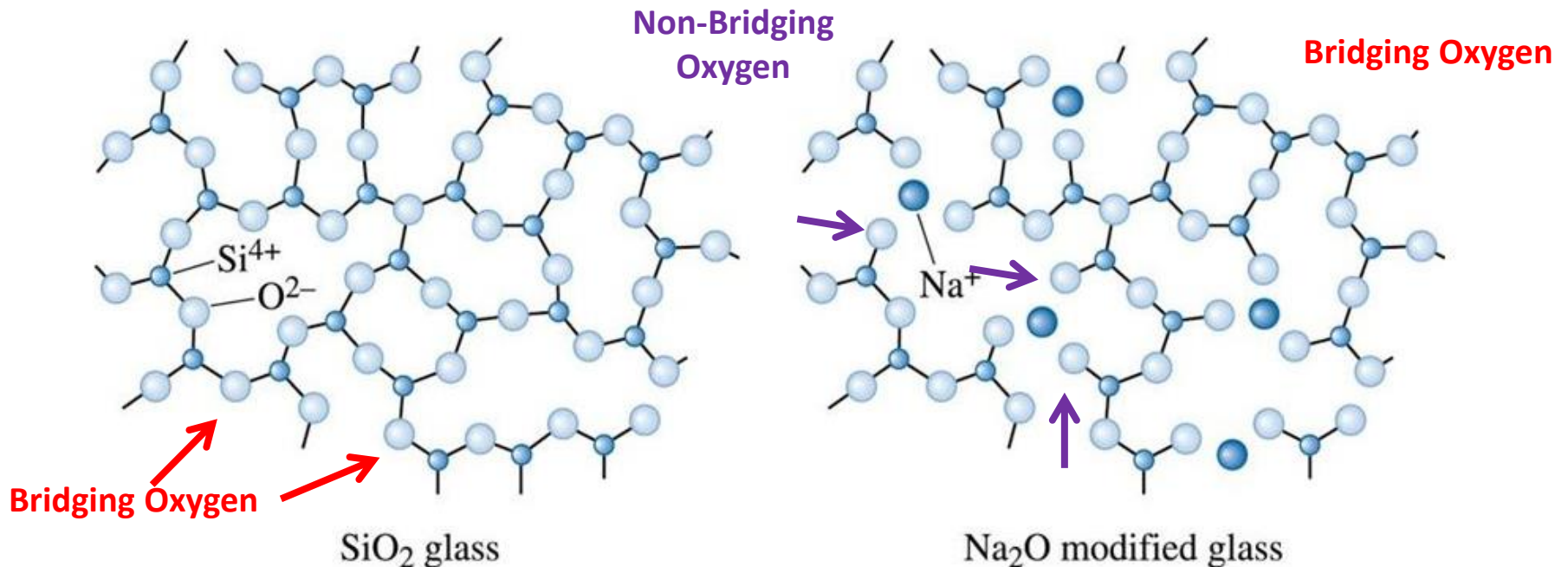
All Rules are Satisfied: SiO_2 forms a glass.



GLASS modifier

STRUCTURE OF GLASSES

Glass modifier disrupts the (3D) glassy network and reduces the ability to form a glass.



↓T_m, ↓T_g

GLASS modifier

2. Consider Magnesia (MgO):

- ionic Mg-O bond
 - Pauling's packing rule:

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

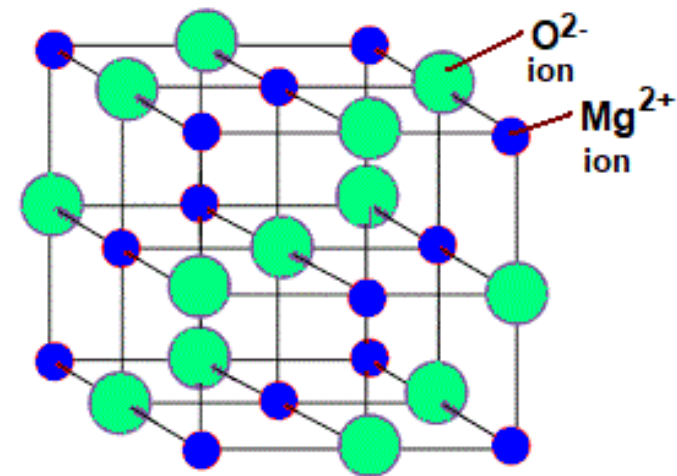
- violates Zachariasen's rule #2.

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

- violates Zachariasen's rule #1.

Crystal structure: edge-sharing polyhedra;

Rules are Not Satisfied: MgO does not form a glass.



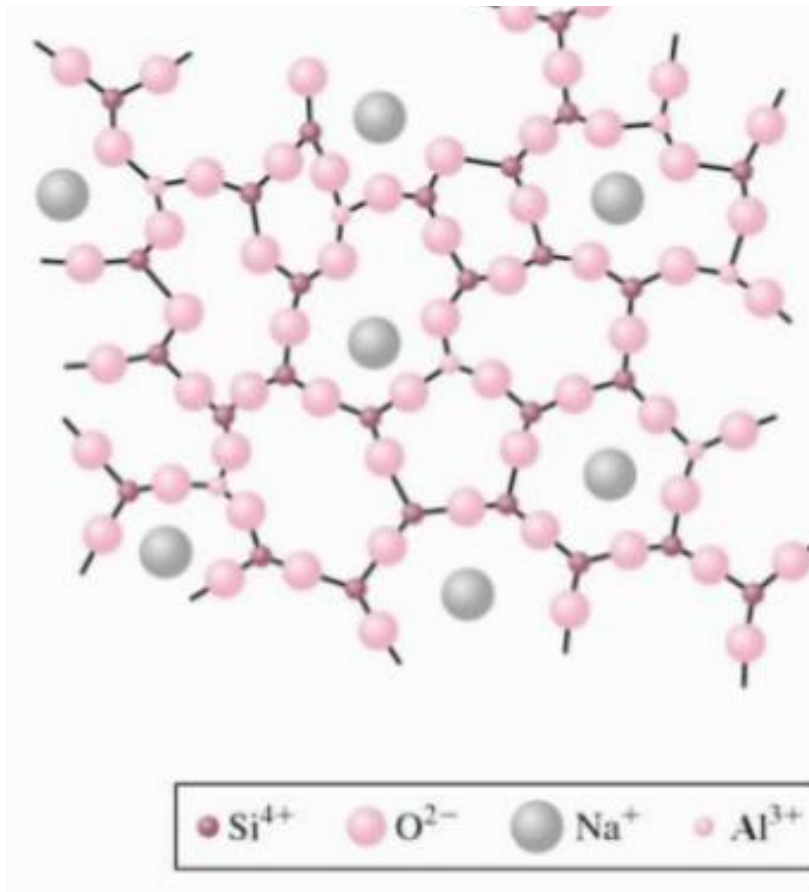
GLASS intermediate

STRUCTURE OF GLASSES

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

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).



Glass intermediates **suture** the (3D) glassy network (**broken by modifiers...**) and increase both T_m and T_g .

$\uparrow T_m, \uparrow T_g$

GLASS intermediate

STRUCTURE OF GLASSES

3. Consider Alumina (Al_2O_3):

- Pauling's packing rule:

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

- octahedral CN preferred in Al_2O_3 .

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

- violates Zachariasen's rule #1.

Al_2O_3 does not form a glass.

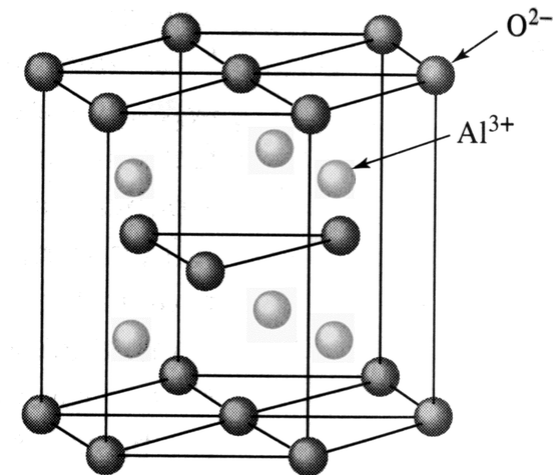
However, in aluminosilicate crystals:

Al-CN = 4

O-CN = 2,

Zachariasen's rules are obeyed → aluminosilicate glasses

Important geological and technological applications



Al^{3+} is an interesting intermediate (with a dual role)!

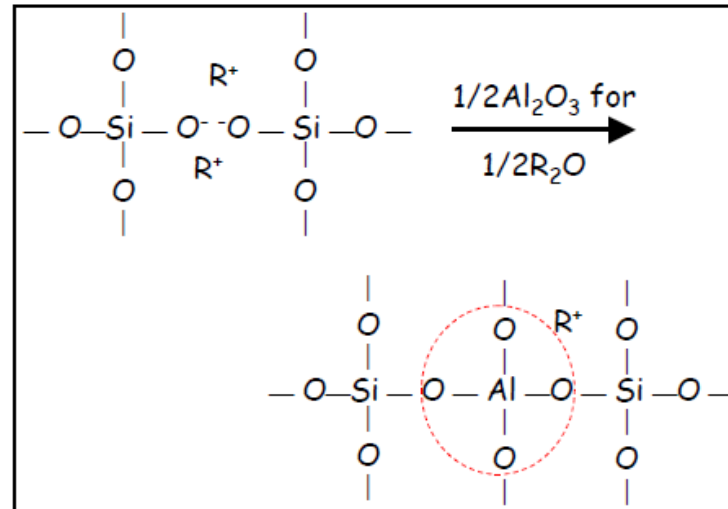
When the concentration of Al_2O_3 is less than (let's say) 3-5 mol%, a substitution of Al^{3+} for Si^{4+} takes place (sss). Here, Al^{3+} acts as intermediate, rebuilding siloxane bonds ($\equiv\text{Al-O-Si}\equiv$) and allowing the presence of a higher level of modifiers in the glass network.

For higher concentrations, Al_2O_3 behaves like a modifier.

GLASS intermediate

STRUCTURE OF GLASSES

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^+

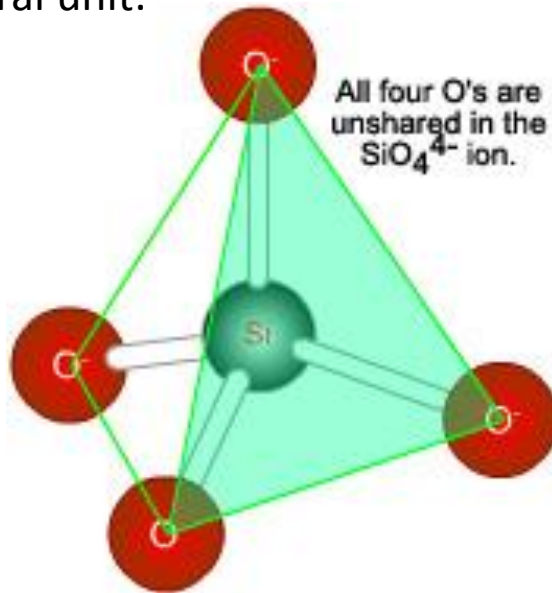
more weakly bound to AlO_4^- than to Si-NBO^-)

Note that this increase in cross-linking occurs up to $[\text{Al}_2\text{O}_3] = [\text{R}_2\text{O}]$; i.e., number of alkalis sufficient to neutralize every AlO_4^- . Further additions of Al_2O_3 ($[\text{Al}]/[\text{R}] > 1$) have different effects on glass properties, likely because of the formation of tri-coordinated oxygens.

NON SILICATE GLASSES

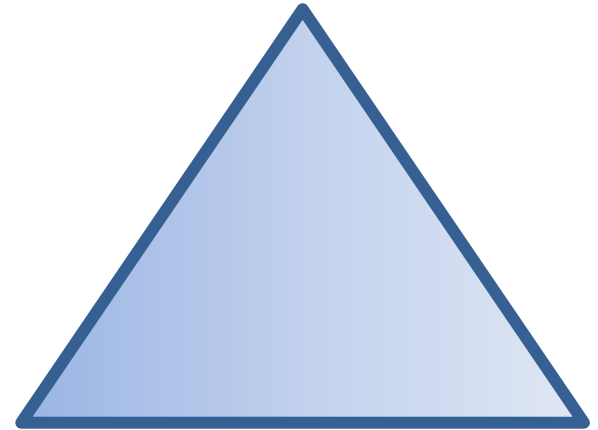
Compounds: **AB_2**

Strutural unit:



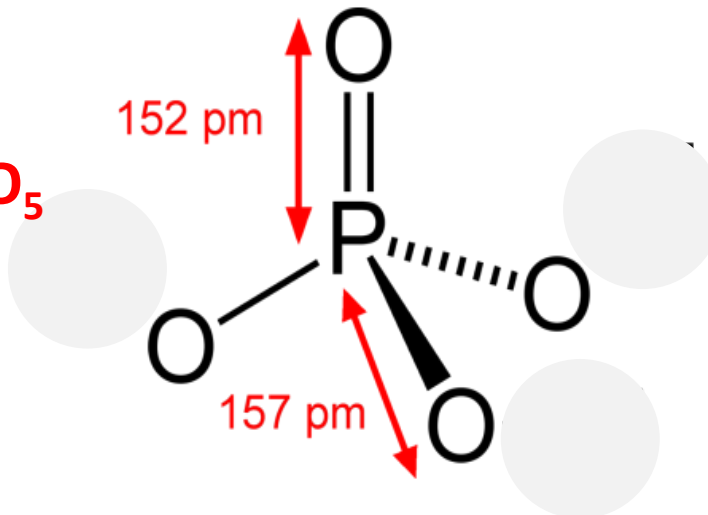
Compounds: **A_2B_3**

Strutural unit:



Compounds: **P_2O_5**

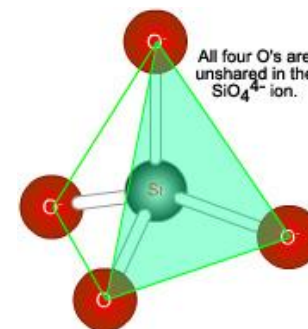
Strutural unit:



NON SILICATE GLASSES

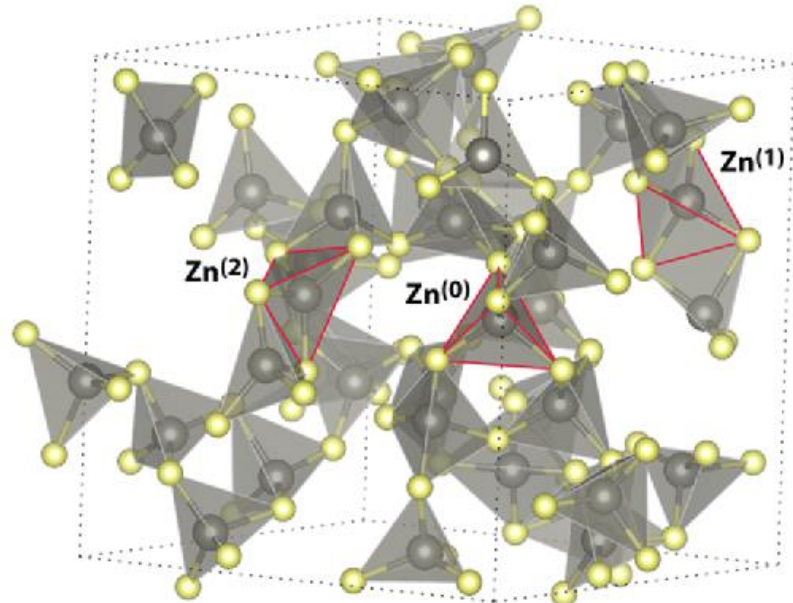
Compounds: **AB₂**

Strutural unit:



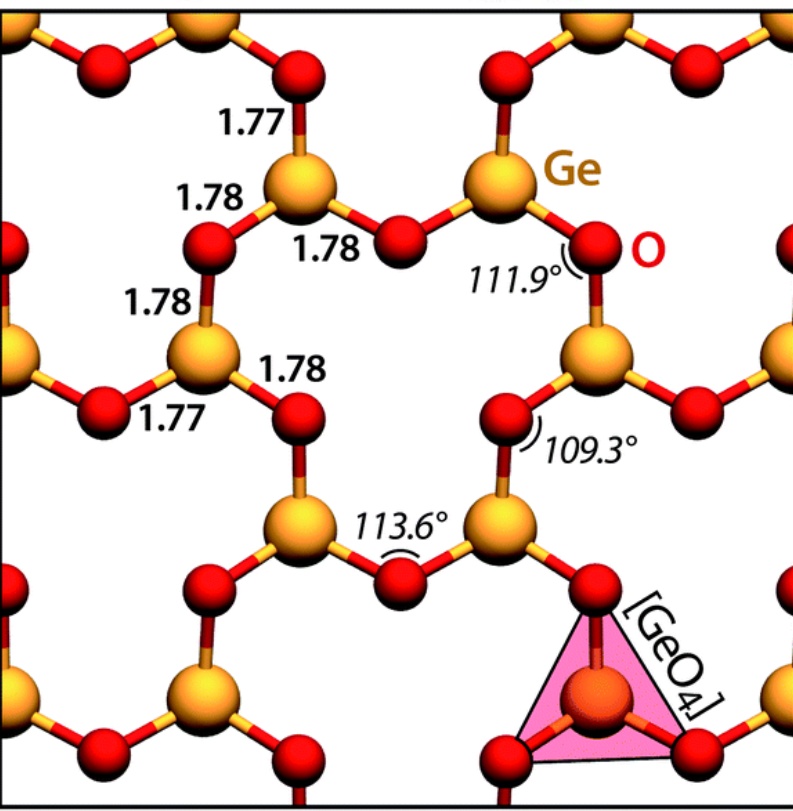
[J. Phys. Chem. B 2016, 120, 17, 4174-4181](#)

DOI: [10.1021/acs.jpcc.6b02452](#)

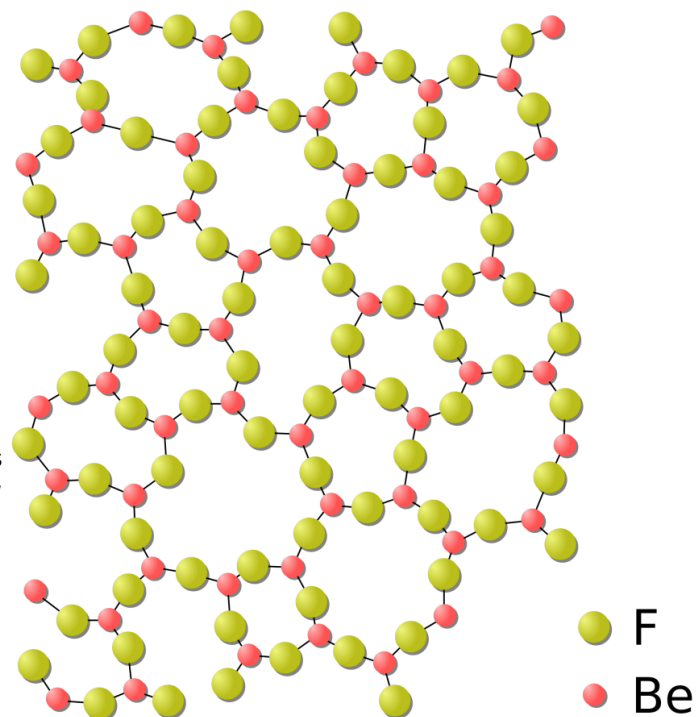


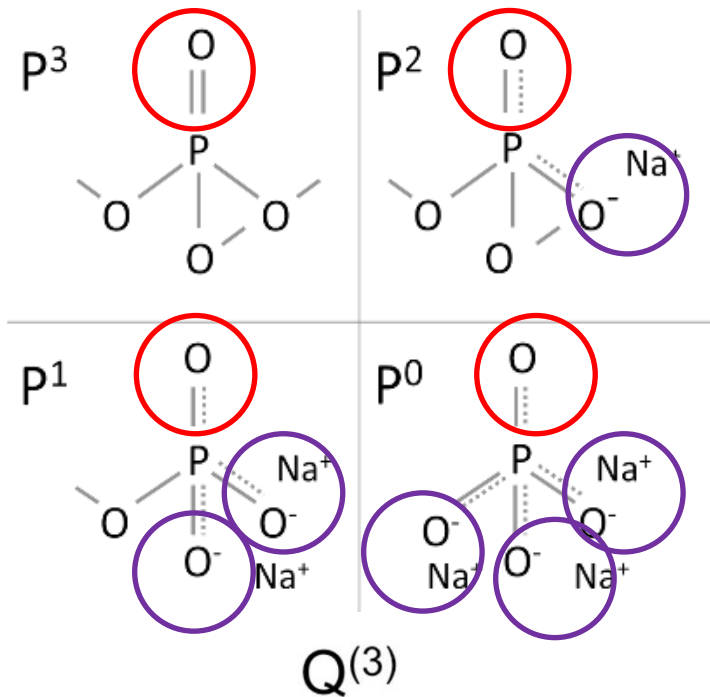
Chem. Sci., 2014,5, 894-903

DOI: 10.1039/C3SC52743C



https://commons.wikimedia.org/wiki/File:BeF2_glas.svg





STRUCTURE OF GLASSES

Compounds: **A₂B₅**

Strutural unit:



2011 / Vol. 1, No. 5 / OPTICAL MATERIALS EXPRESS 845

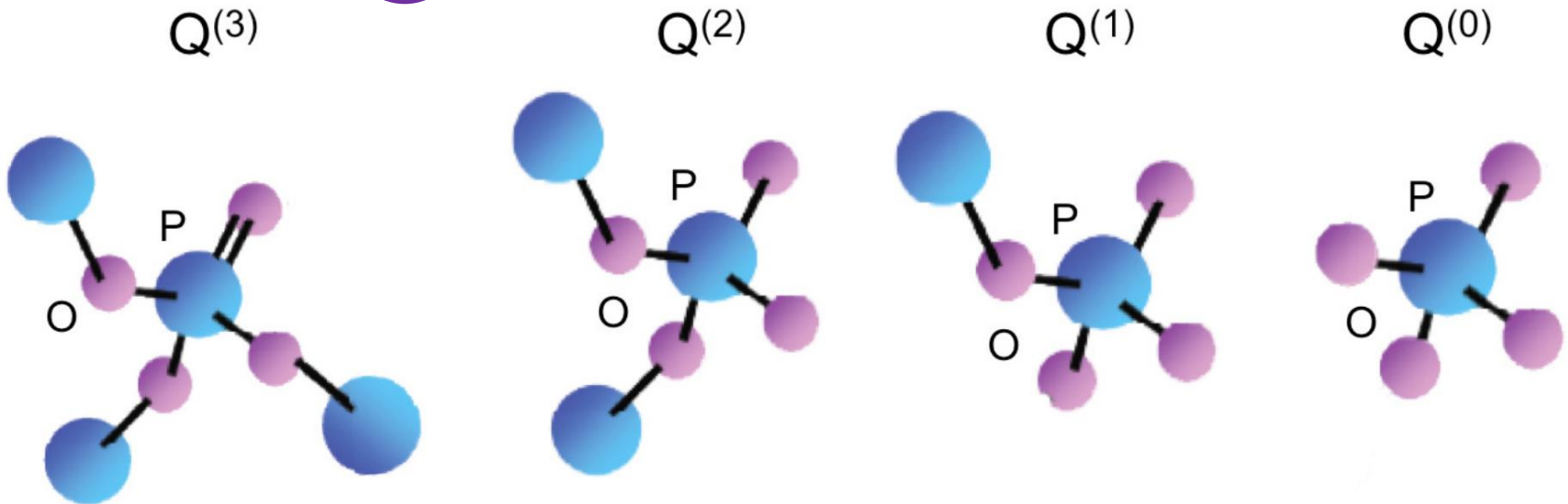
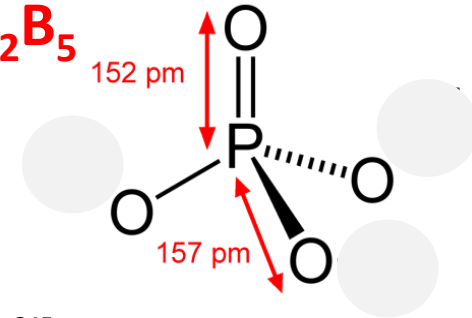
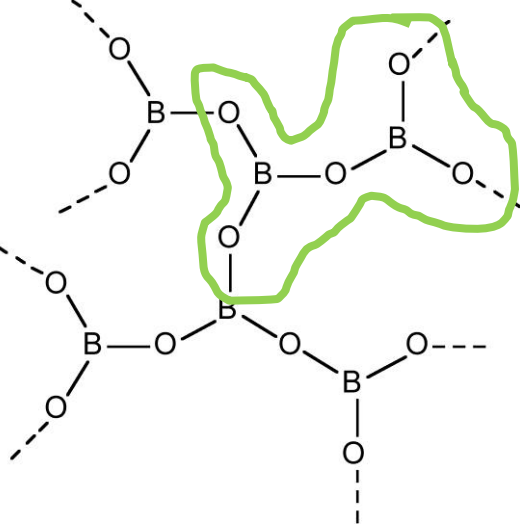


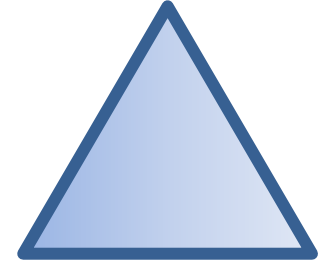
Fig. 1. Phosphate tetrahedral units – oxygen atoms (pink) connected to a phosphorus atoms (blue); Q³ crosslinking units; Q² middle units; Q¹ end units; Q⁰ isolated units.



STRUCTURE OF GLASSES

Compounds: A_2B_3

Structural unit:



Amorphous B_2O_3 is composed of **triangular BO_3 units**, probably interconnected locally into boroxyl group.

Alkali additions do not act as modifiers, but instead **increase connectivity by forming tetrahedral BO_4 units with local charge compensation by the alkali.**

The formation of compact tetrahedra causes an increase in density and a decrease in the thermal expansion coefficient (Boron anomaly).

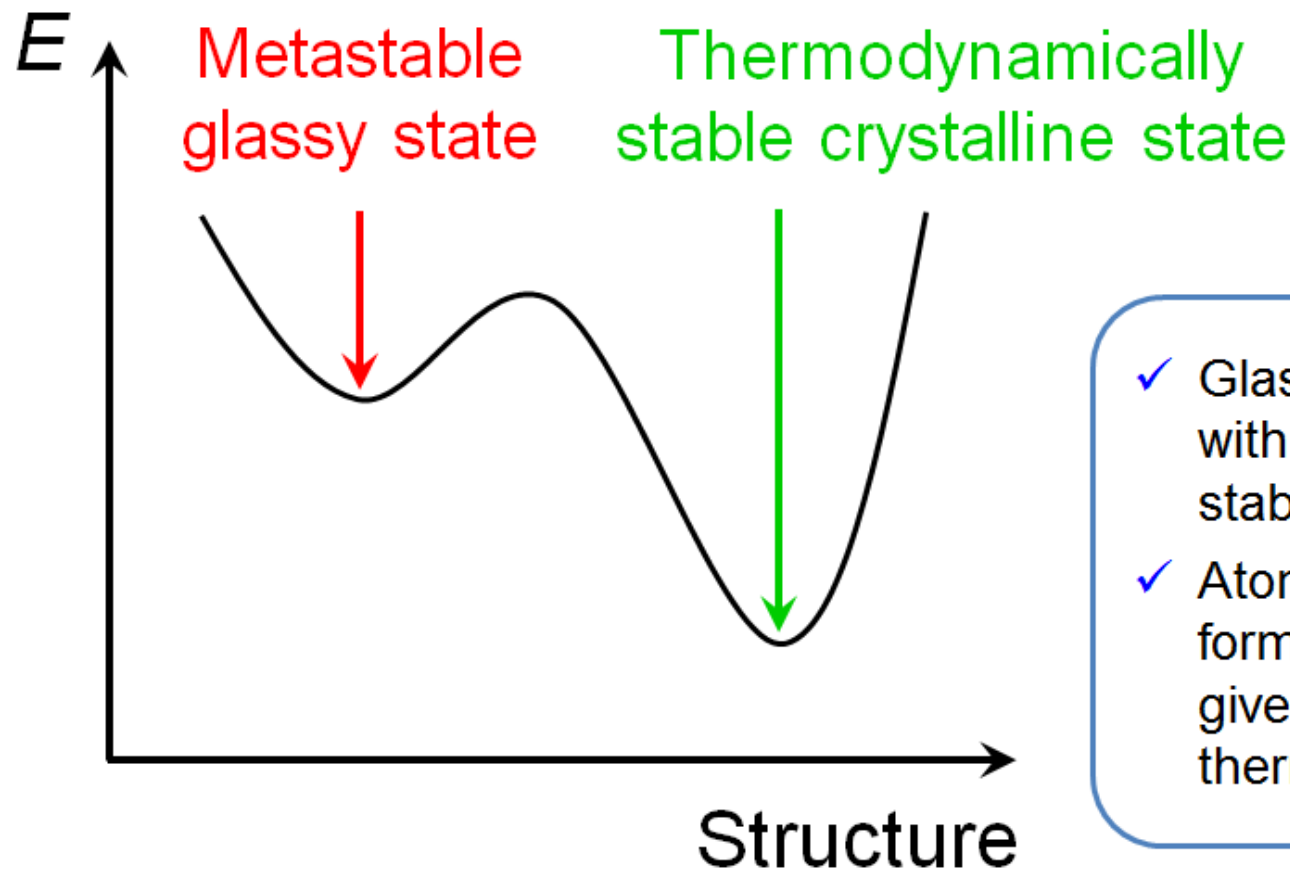
Pyrex™ and **Kimax™** are sodium borosilicates in which the alkali/B ratio is close to that of minimum thermal expansion coefficient.

Vycor™ is a glass in which a phase-separation occurs at 500-600°C into high borate and high silica phases.

GLASS METASTABILITY

What is glass (amorphous solid)?

- A **metastable** solid with no long-range atomic order

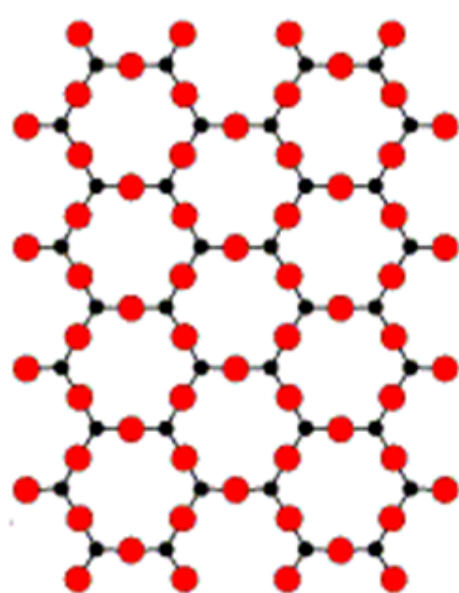


- ✓ Glasses are metastable with respect to their stable crystalline phase
- ✓ Atoms can rearrange to form a more stable state given enough time and thermal energy

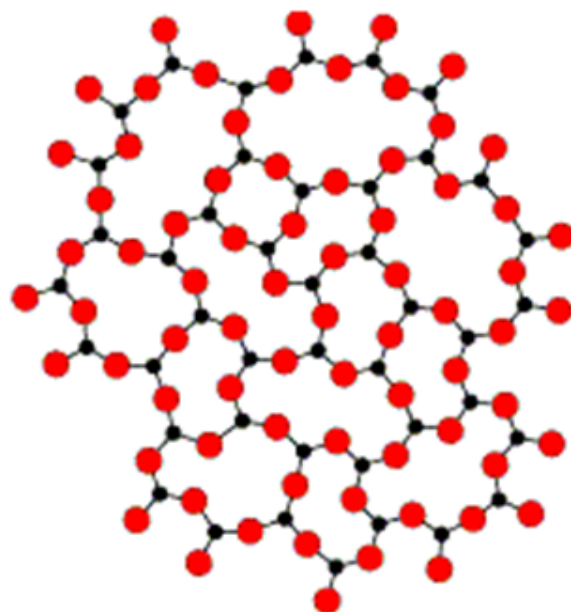
What is glass (amorphous solid)?

- A metastable solid with **no long-range atomic order**

Consider a fictitious A_2O_3 2-D compound:



A_2O_3 crystal

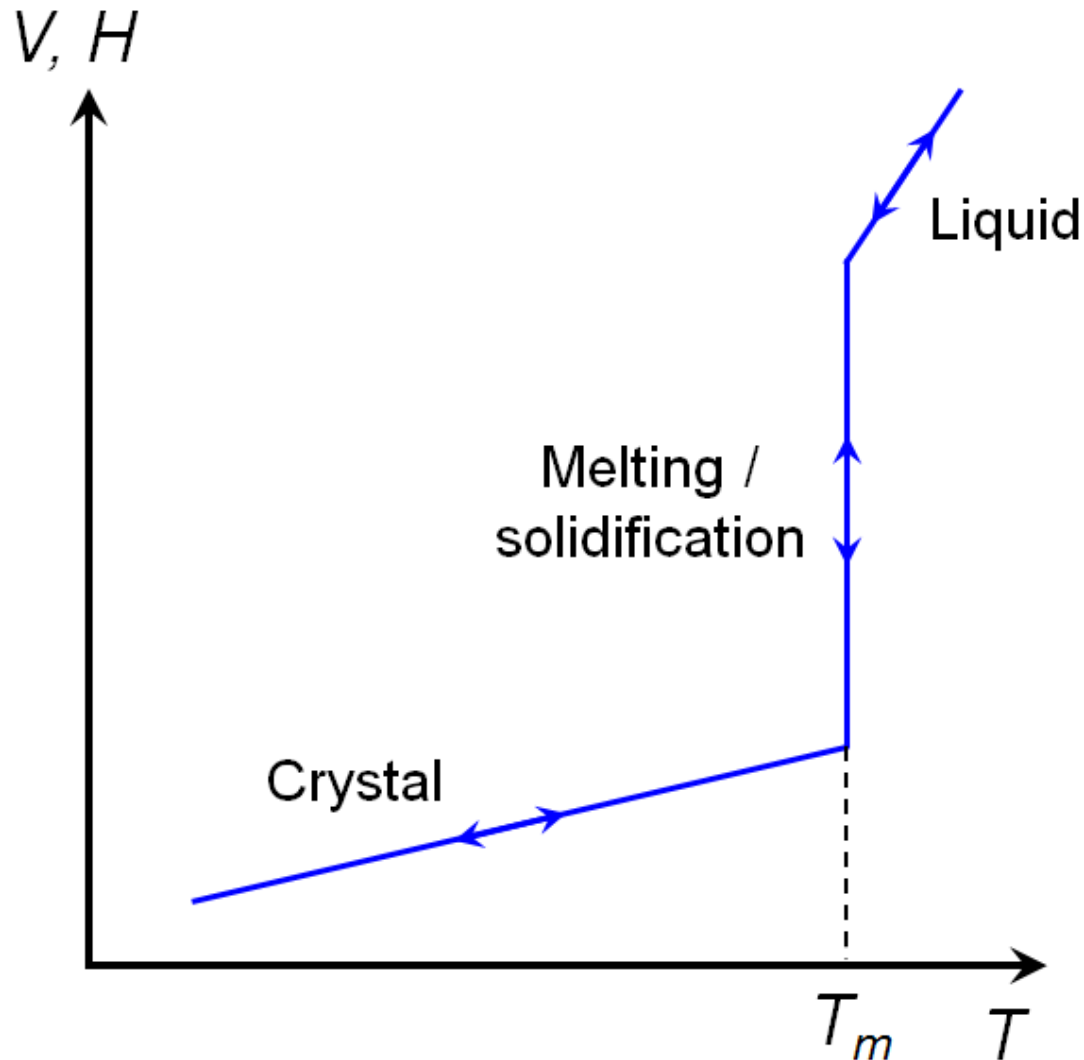


A_2O_3 glass

- ✓ Short-range order is preserved (AO_3 triangles)
- ✓ Long-range order is disrupted by changing bond angle (mainly) and bond length
- ✓ Structure lacks symmetry and is usually isotropic

Zachariasen's Random Network Theory (1932)

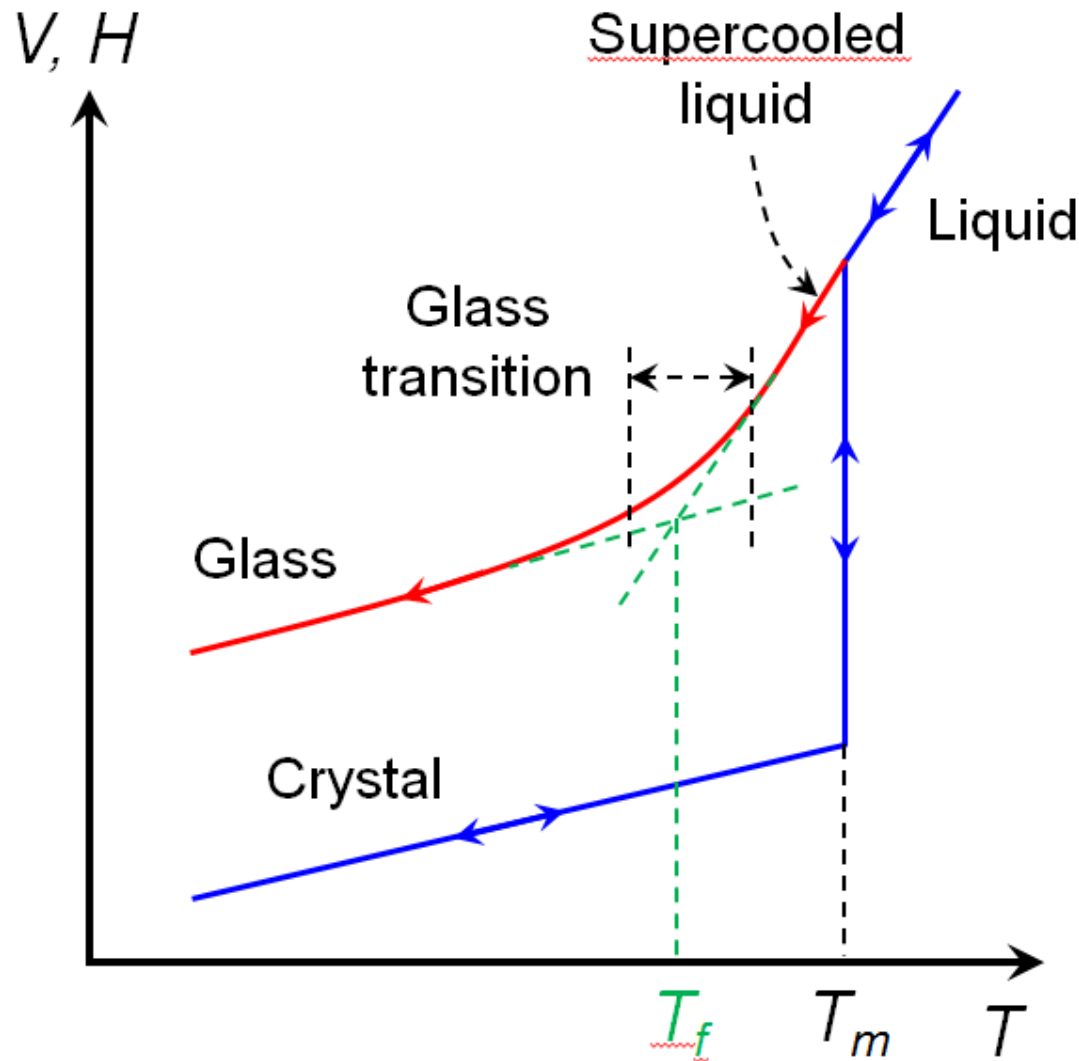
Glass formation from liquid



When the system is kept in thermal equilibrium:

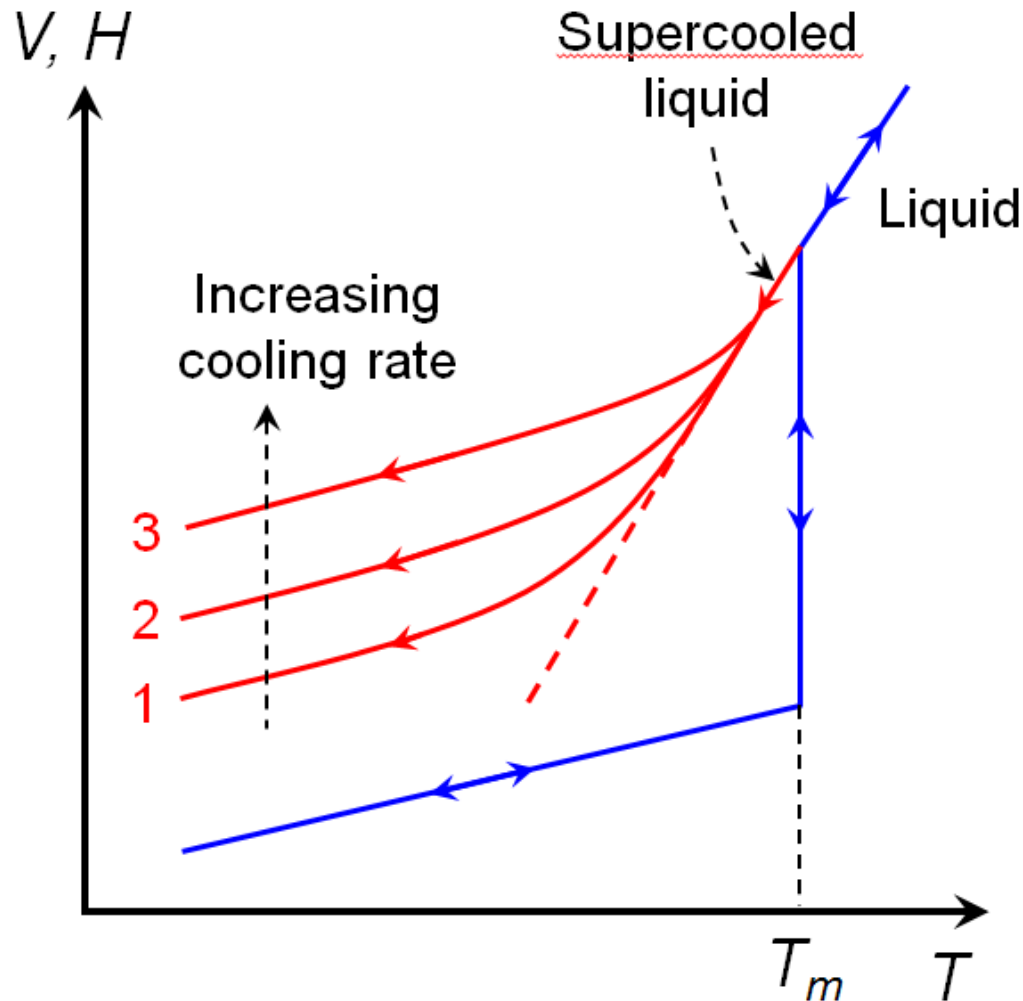
- ✓ First-order liquid-solid phase transition
- ✓ Discontinuity of extensive thermodynamic parameters (e.g., V and H)
- ✓ Reversible process

Glass formation from liquid



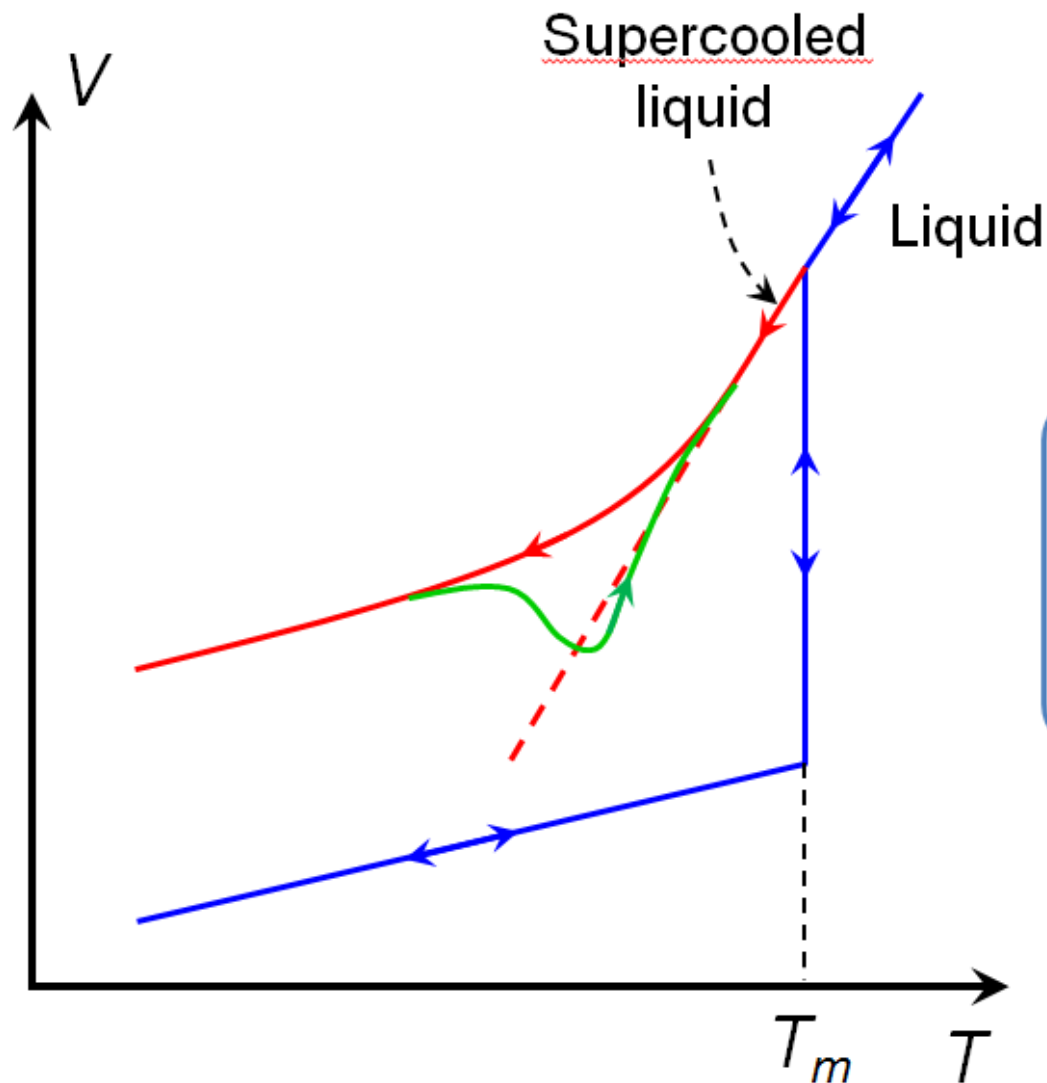
- ✓ Supercooled liquid transforms to the glassy state when crystallization is kinetically suppressed
- ✓ Extensive variables remain **continuous** during glass transition
- ✓ The glassy state is **different** from super-cooled liquid
- ✓ T_f : Fictive temperature

Glass formation from liquid



- ✓ Glasses obtained at different cooling rates have different structures
- ✓ With increasing cooling rate:
 - ❖ $V_1 < V_2 < V_3$
Free volume increases
 - ❖ $H_1 < H_2 < H_3$
Configurational entropy increases
 - ❖ $T_{f,1} < T_{f,2} < T_{f,3}$

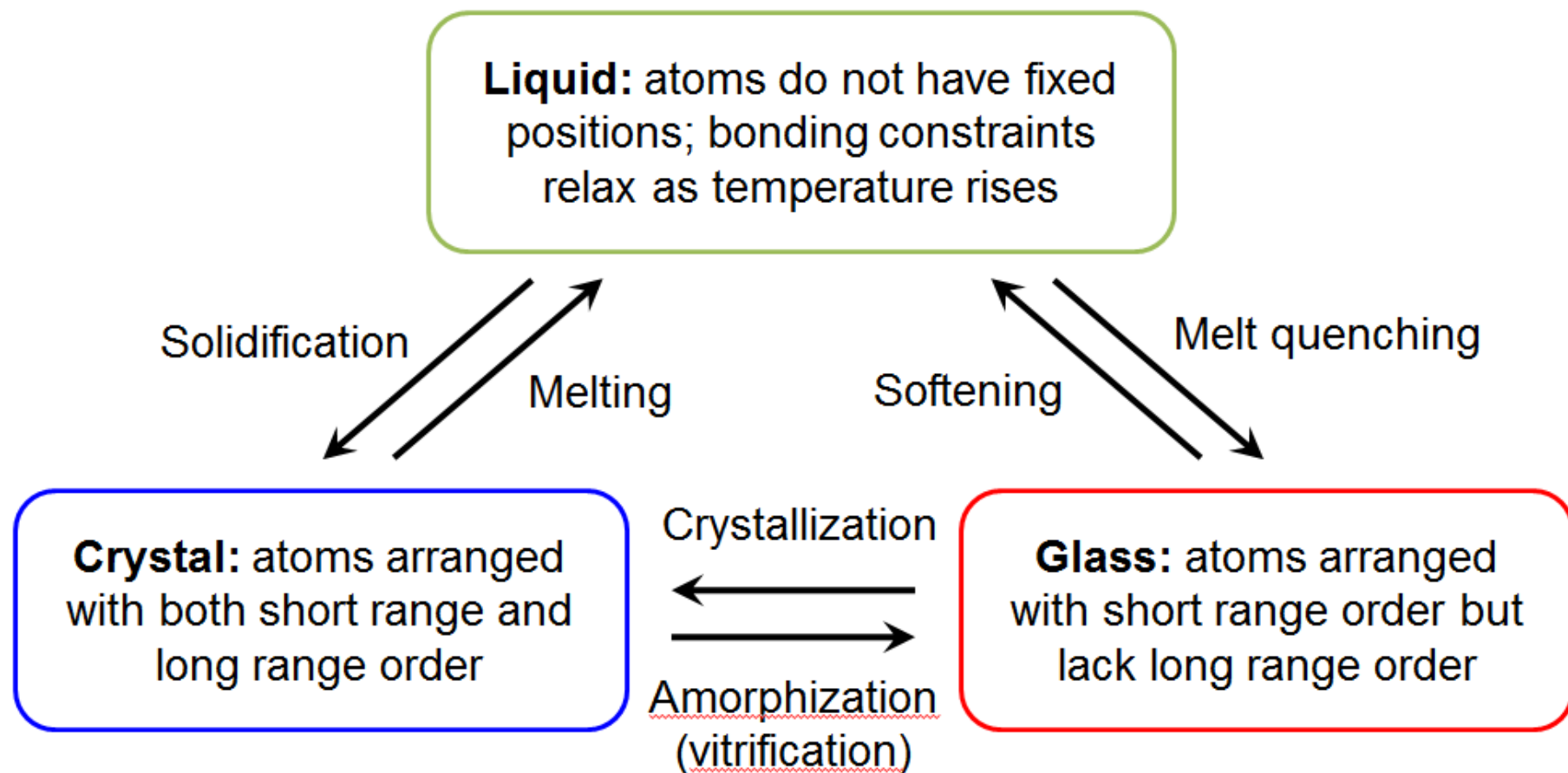
Glass formation from liquid



The heating curve never retraces the cooling curve during glass transition due to structural relaxation

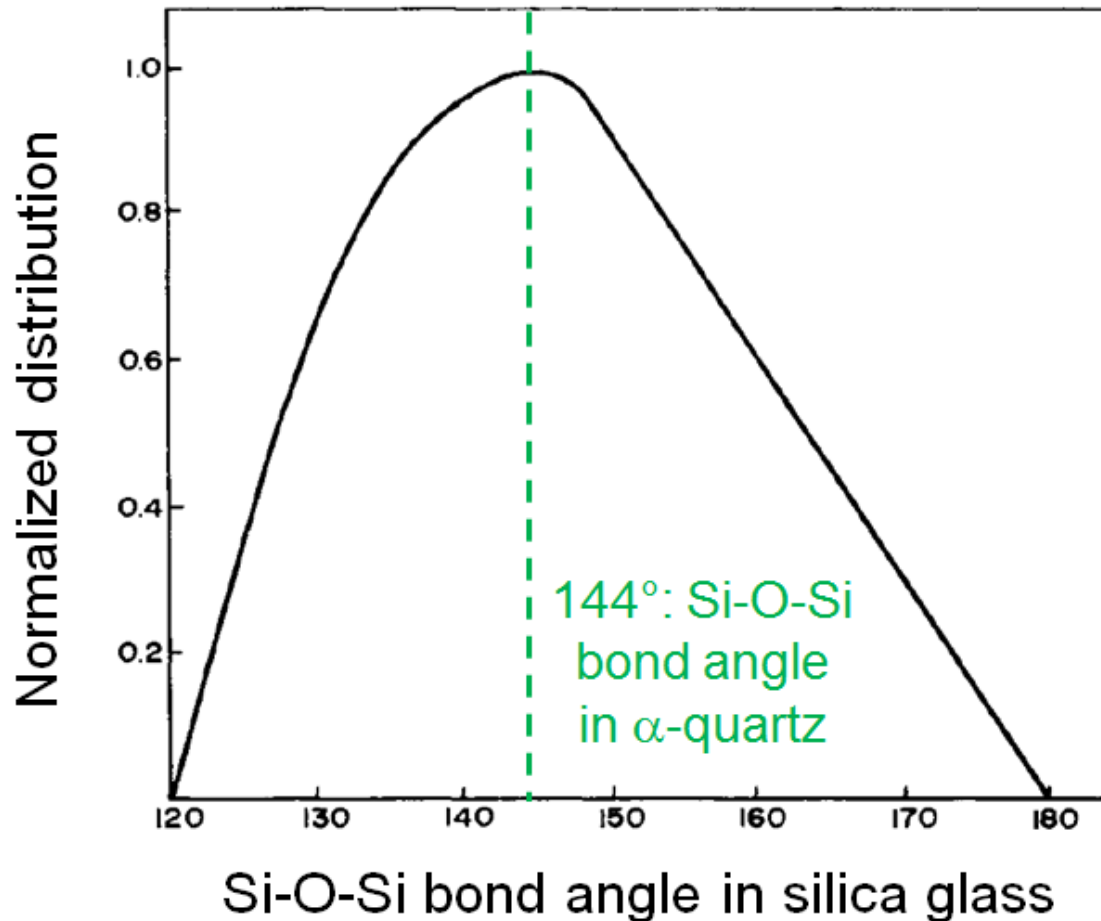
What is glass (amorphous solid)?

- A **metastable** solid with **no long-range atomic order**



What is glass (amorphous solid)?

- A **metastable** solid with **no long-range atomic order**

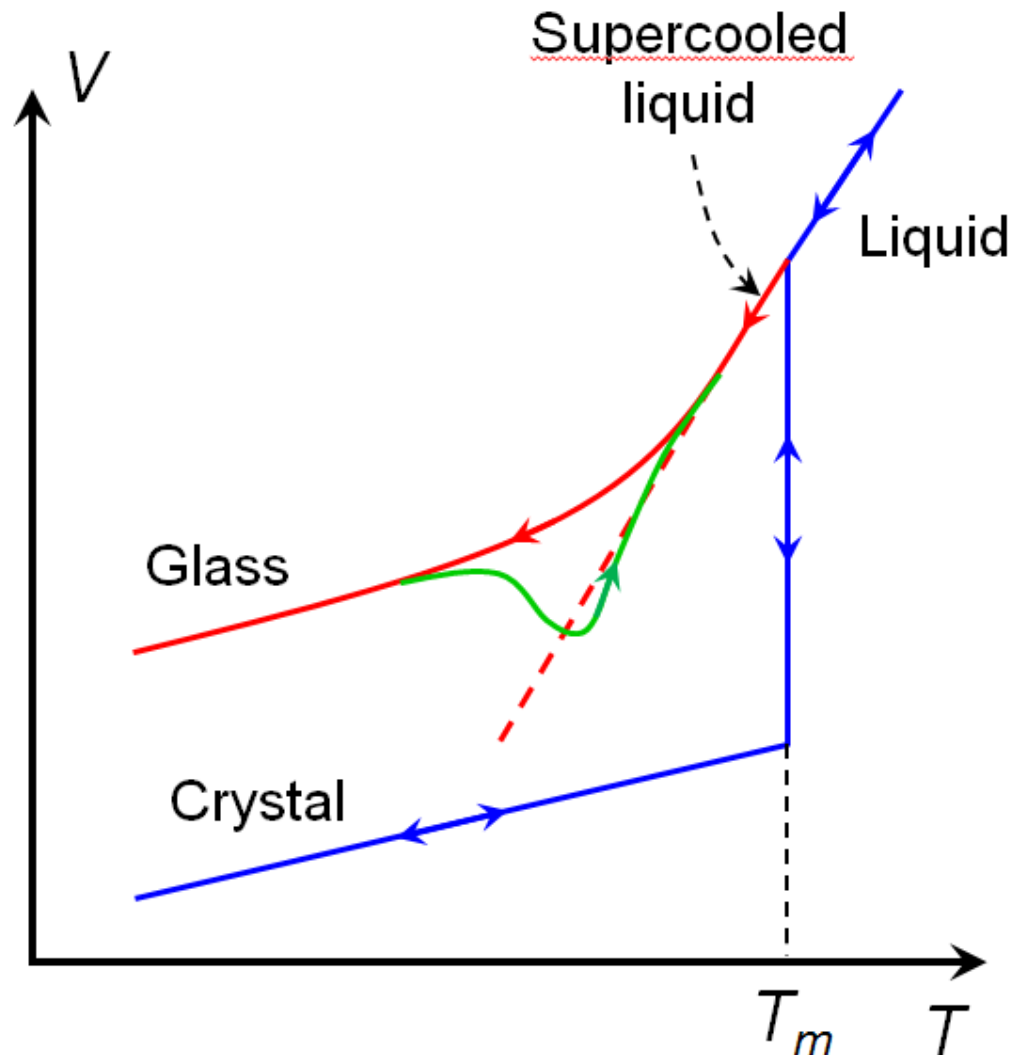


Si-O-Si bond-bending constraint is relaxed at the forming temperature of silica glass

Si-O-Si bond angle distribution in silica glass measured by XRD

J. Appl. Cryst. **2**, 164 (1969)

Summary



- The amorphous state is metastable
- Amorphous structures possess short-range order and lack long-range order
- Amorphous materials can be obtained from liquid by melt quench
- Melt quench is a continuous, irreversible process involving phase change
- Glass properties depend on their thermal history

STRUCTURE OF GLASSES

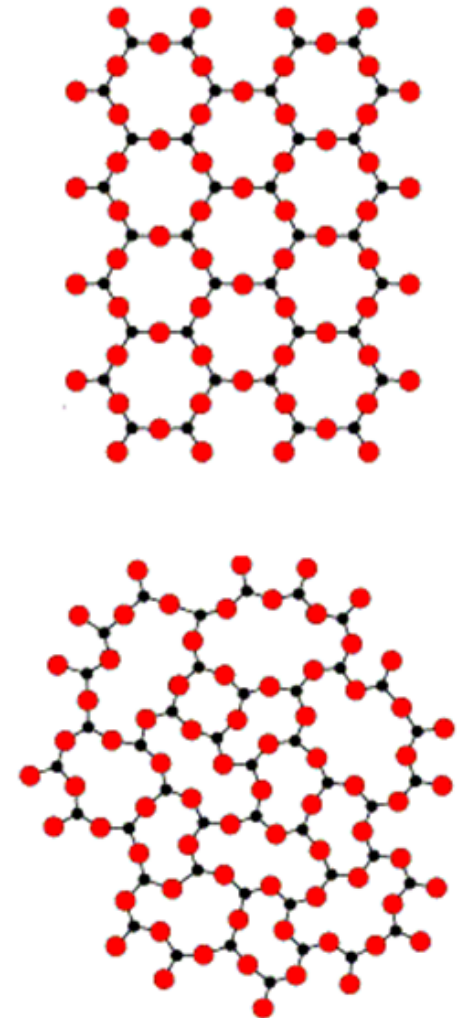
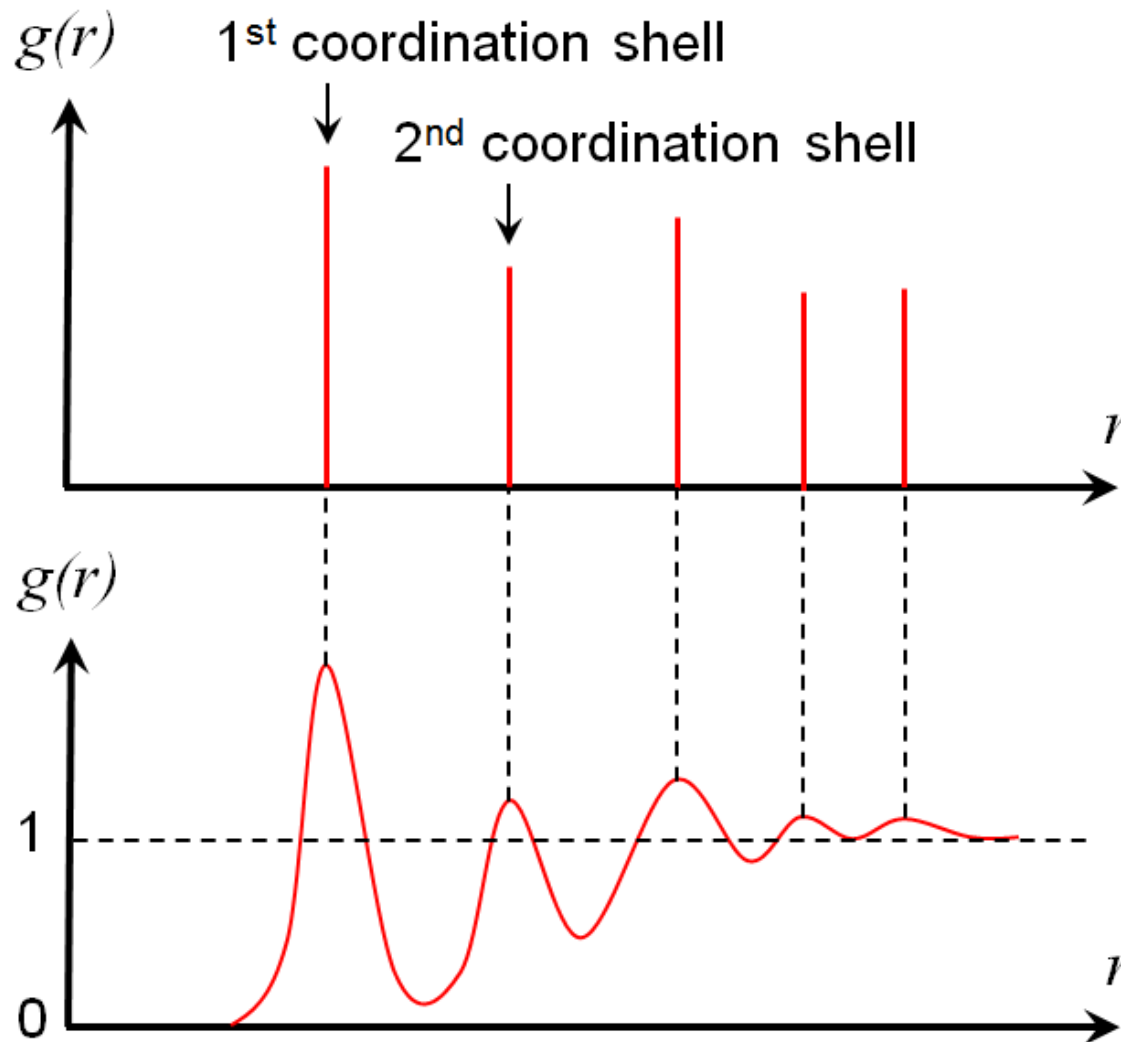
1. Coordination of network cations/glass formers
 - Network building blocks
 - Short range order
 - Determined by a variety of spectroscopic probes
2. Bond Angle Distributions
 - Experimentally difficult (diffraction)
3. Network Connectivity
 - How are neighboring glass forming polyhedra linked?
 - Bridging 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

ADITIONAL INFORMATION

Quantitative description of glass structure

- Structural descriptions of amorphous materials are always statistical in nature
- Pair distribution function (PDF): $g(r)$
 - Consider an amorphous material with an average number density of atom given by:
$$\rho = n/V$$
 n : number of atoms V : material volume
 - The number density of atoms at a distance r from an origin atom is given by $\rho \cdot g(r)$
 - When $r \rightarrow 0$, $g \rightarrow 0$
 - When $r \rightarrow \infty$, $g \rightarrow 1$

PDFs of ideal (hard sphere) crystals vs. glasses



Quantitative description of glass structure

- Pair correlation function $h(r)$

- $h(r) = g(r) - 1$

- Radial distribution function (RDF): $J(r)$

- $J(r) = 4\pi r^2 \rho \cdot g(r)$

- $J(r)dr$ gives the number of atoms located between r and $r + dr$ away from the origin atom

- The area under the RDF curve gives the number of atoms

- Reduced radial distribution function (rRDF): $G(r)$

- $G(r) = 4\pi r^2 \rho \cdot [g(r) - 1] = 4\pi r^2 \rho \cdot h(r)$

Further reading

- **Introduction to Glass Science and Technology.** J. E. Shelby, 2nd Ed RSC PaperBacks (2005)
- **Les Verres et l'État Vitreux.** J. Zarzycki Masson (1997)
- **Glass Science.** R. H. Doremus Wiley Interscience (1994)
- **Overall aspects of non-traditional glasses. Synthesis, properties and applications.** H C. Vasconcelos, M. C. Gonçalves (eds) **Bentham Science Publishers** (2016)
- **Glass.** M. C. Gonçalves. *In: Materials for Construction and Civil Engineering: Science, Processing, and Design* p. 335-395 M. C. Gonçalves, F. Margarido (eds) Springer, New York (2015)