Advanced Glass Science
(4016101)

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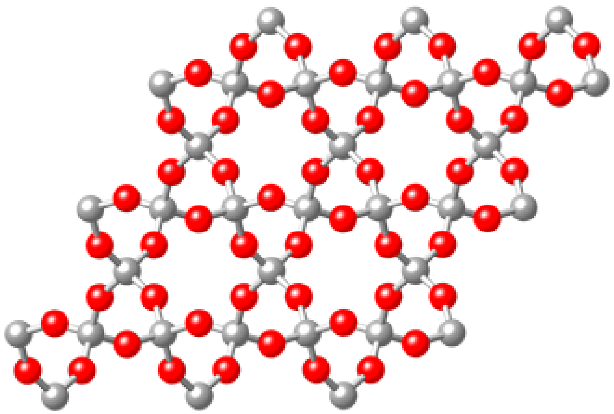
Course Outine:

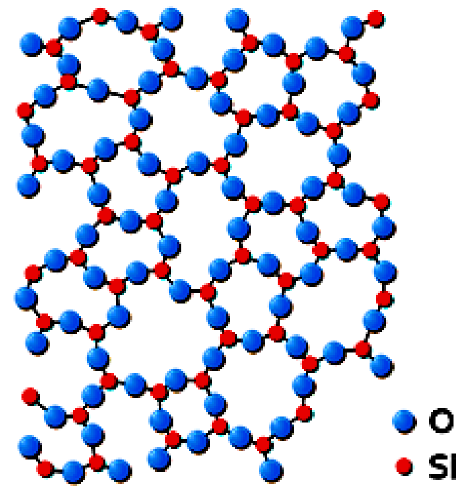
Week 1:
- Crystal and glass materials
- Definition of glass
- Glass formation
- Type of glass
- Function in glass structure
- Structure of glass
- Preparation of glass

Crystal and glass materials

A **crystal** or **crystalline solid** is a solid material whose constituent atoms ,molecules ,or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions .



Crystal Silica (SiO_2)



An **amorphous** or **non-crystalline solid** is a solid that lacks the long-range order characteristic of a crystal.

In part of the older literature, the term has been used synonymous with glass . Nowadays, "amorphous solid" is considered to be the overarching concept, and "glass" the more special case: A glass is an amorphous solid that transforms into a liquid upon heating through the glass transition.

Definition of glass

-A state of matter

- Properties of crystal + liquids
- Mechanical rigidity of crystal ***but*** the random disordered arrangement of molecules that characterizes liquids
- Formation "melting crystalline materials at high temperatures"
- When cools, "the atoms are locked into a random (disordered) state ***before*** they can form into a perfect crystal arrangement"

*One of the most important properties of glasses is ***transparency***,
➡complete lack of grain boundaries or inclusions, which would cause the ***reflection of light***

Definition of glass

- The most widely used definition of a glass, purposed by the ASTM (The American Society for Testing Materials)
"***a glass is an inorganic product of fusion, which has cool to a regid condition without crystallising***"

- a glass or a substance in the glassy or vitreous state, is a material, form by ***cooling from the normal liquid state***, which shown no ***discontinuous changes*** but has become more or less rigid through a progressive increase in its viscosity.

Glass formation

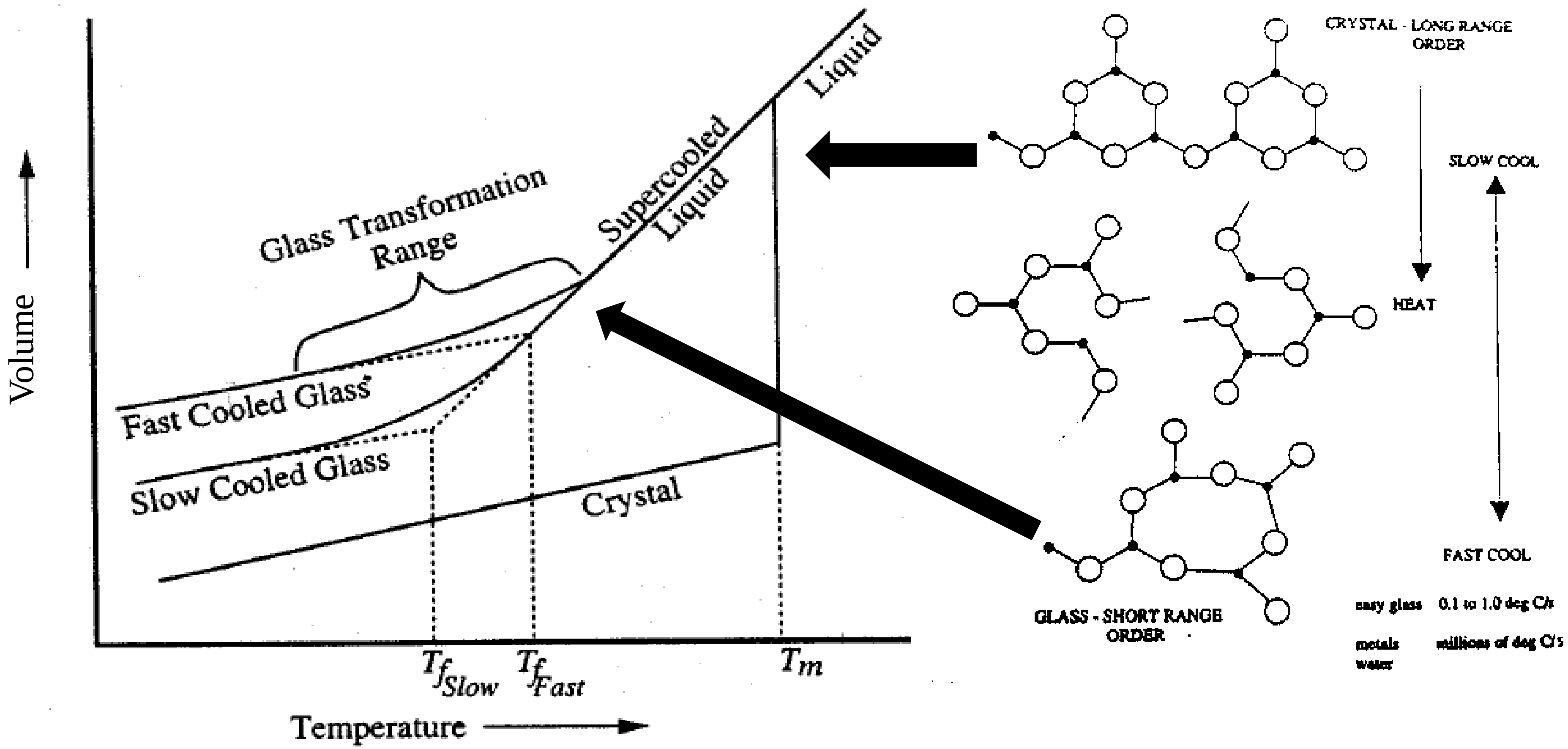


Fig. 1 Specific Volume-Temperature Diagram

Summary (Crystal and glass materials)

Table 1. Comparison different of crystal and glass

Crystal	Glass
Crystalline structure	Amorphous structure
High atomic ordering	Atomic disordering
Size and shape limit in preparation	Can prepare in wide range of size and various shape
Low dopant concentration limit (High dopat concentration can disturb crystalline structure)	Dopant concentration limit higher than crystal

Type of glass

1. Fused silica (SiO_2 99.99%)

- High temperature stability
- Low thermal expansion
- High thermal shock resistance
- Excellent chemical durability and purity
- Good optical transmission in the ultraviolet range
- Produce at high melting temperature
- Expensive
- Applications: Lamp envelopes, Cuvettes, Optical components

A sphere manufactured by NASA out of fused quartz for use in a gyroscope in the Gravity Probe B experiment. It is one of the most accurate spheres ever created by humans, differing in shape from a perfect sphere by no more than 40 atoms of thickness. It is thought that only neutron stars are smoother.

Type of glass

2. Sodium calcium silicate or Soda lime silicate ($Na_2O+CaO+SiO_2$)

- Cheap and weather well
- Easily method and formed
- Low thermal and chemical resistance
- High thermal expansion
- Bottoms, windows

Na_2O_3 = Soda ash
CaO = Lime stone

Type of glass

3. Borosilicate (B_2O+SiO_2)

- Lower thermal expansion
- Better thermal shock resistance
- Improve chemical durability
- Applications: head lamps, cooking ware and laboratory apparatus






Type of glass

4. Aluminosilicate (Al_2O+SiO_2)

- Chemical durability
- Resistance to devitrification
- Low thermal coefficient
- High refractive index
- Higher temperature and greater strength in cooking ware
- Applications: Vacuum electronic, Space-vehicle windows Display

Type of glass

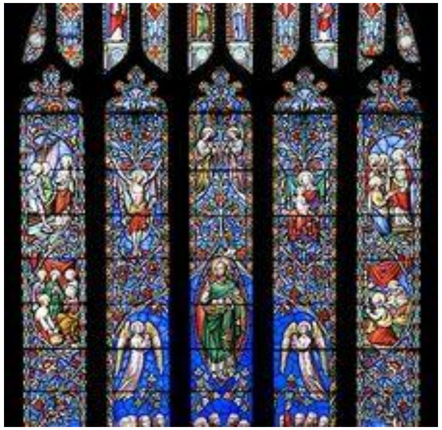
4. Alkali-Earth Aluminosilicate ($CaO+Al_2O+SiO_2$)

- High refractive index (nearby lead glass)
- Chemical durability
- Easy manufacturing (better lead glass)
- Applications: crystal glass

Type of glass

5. Lead glasses (Pb_2O_3)

- High refractive index
- Greater density as lamp envelopes
- Toxicity
- Applications: Optical glass

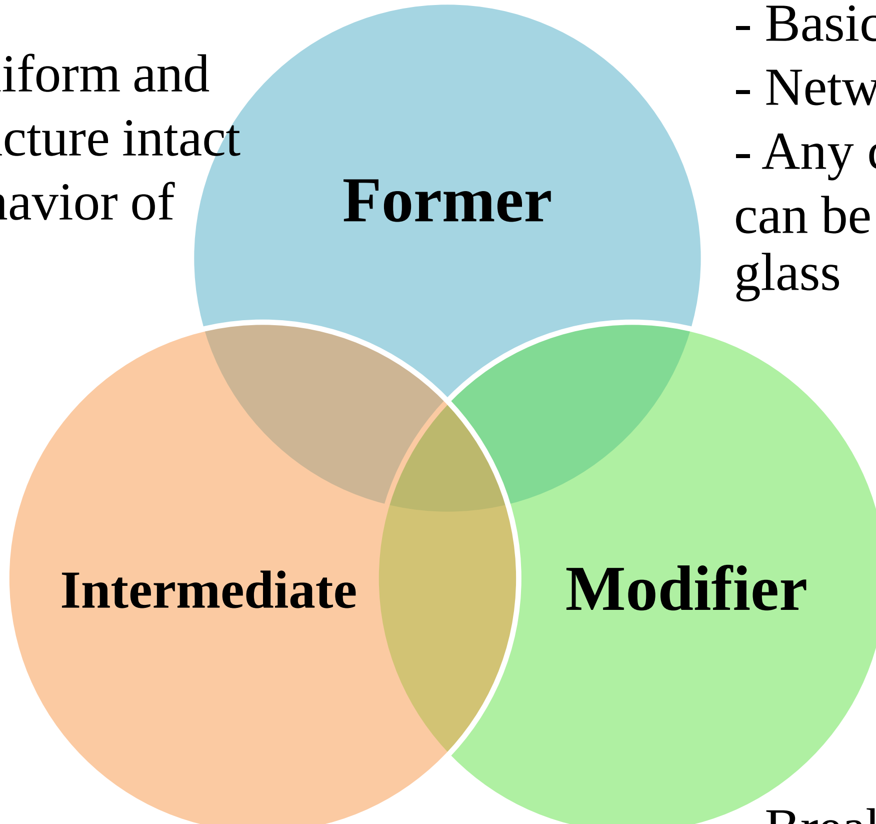


Composition of glass (Raw materials)

Raw materials	Advantages
SiO_2	Good thermal and chemical durability
B_2O_3	Low thermal expansion
CaO	Increase chemical durability
Na_2O	Reduce melting temperature
Al_2O_3	Increase chemical durability and reduce corrosion
Fe_2O_3	Increase transparency of glass (and make green glass)
PbO	Increase physical properties and refractive index of glass
Transition	Color glass
Rare earth	Luminescence

Function in glass structure

- Make the glass uniform and keep its special structure intact
- May show the behavior of former or modifier



- Basic ingredients
- Network former glass
- Any chemical compound that can be melted and cooled into a glass

- Break bond of glass former
- Reduce melting temperature
- Reduce viscosity

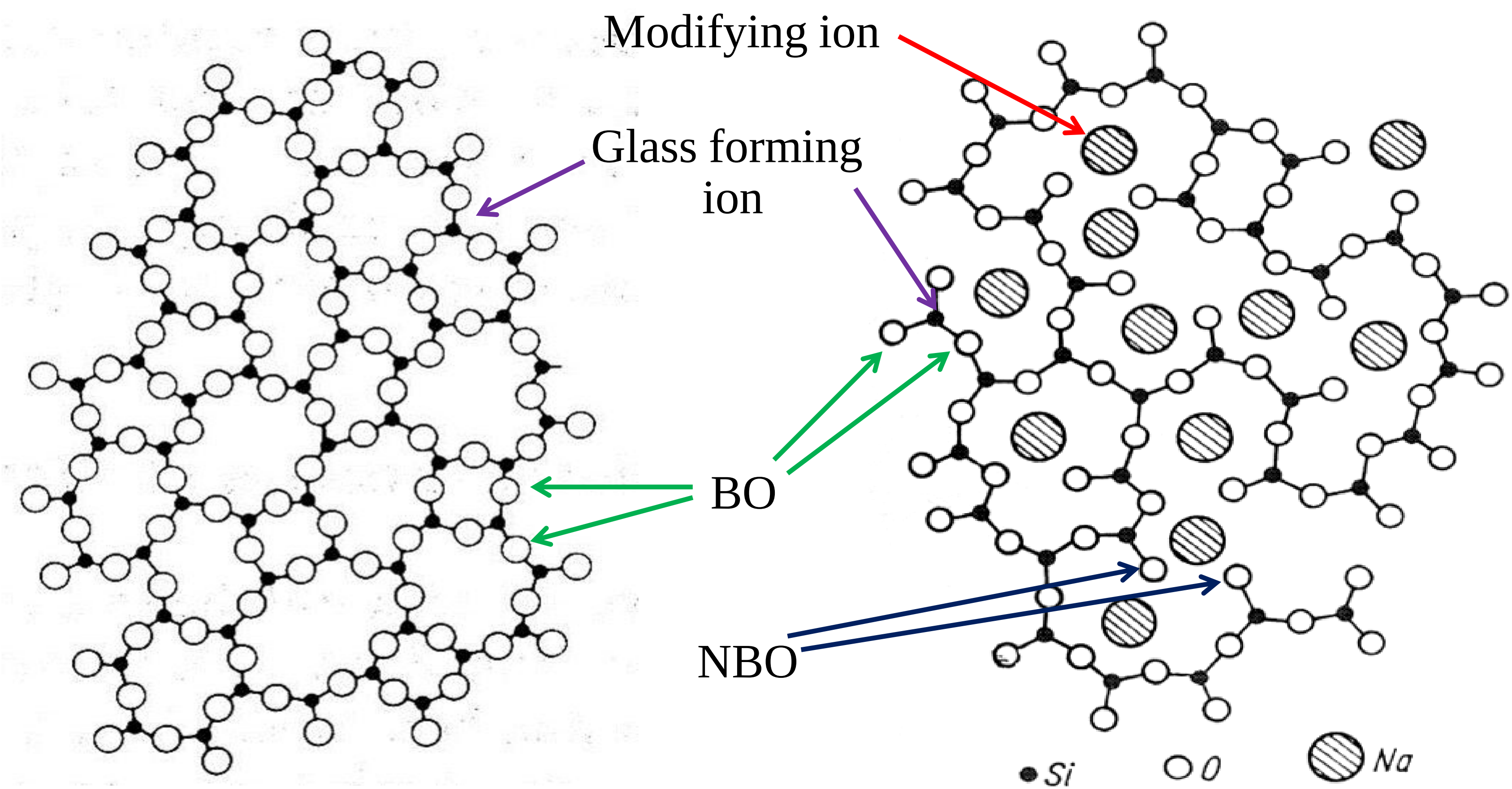
Function in glass structure

Former	Modifier
Si_2O	Li_2O, Na_2O, K_2O (Alkaine group)
B_2O_3	MgO, CaO, SrO, BaO (Alkaline-earth group)
P_2O_5	
TeO_2	

Modifier + Former

A. $20Li_2O + 80Si_2O$ = Lithium silicate
B. $5MgO + 15Li + 80B_2O_3$ = Magnesium lithium borate
C. $10CaO + 15SrO + 75P_2O_5$ = Calcium strontium phosphate
D. $20PbO + 80TeO2$ = Lead telurate
E. $10PbO + 25B_2O_3 + 65SiO_2$ = Lead boro-silicate
F. $20Bi_2O_3 + 20B_2O_3 + 60TeO_2$ = Bismuth boro-telurate
G. $10CaF_2 + 90P_2O_5$ = Calcium fluorophosphate
H. $7Gd_2O_3 + 15CaF_2 + TeO_2$ = Gadolinium calcium tellurate

Function in glass structure



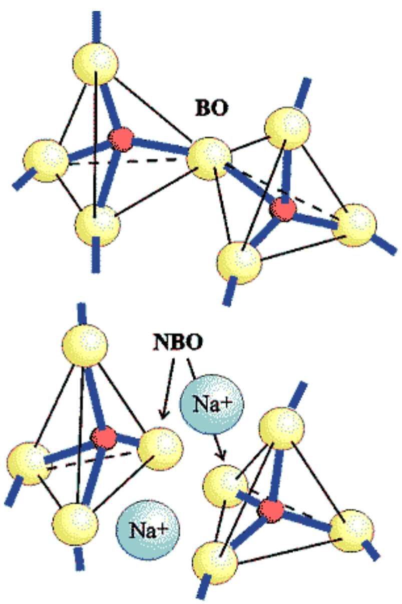
(a) Before *modifier* insert **(b) After *modifier* insert**

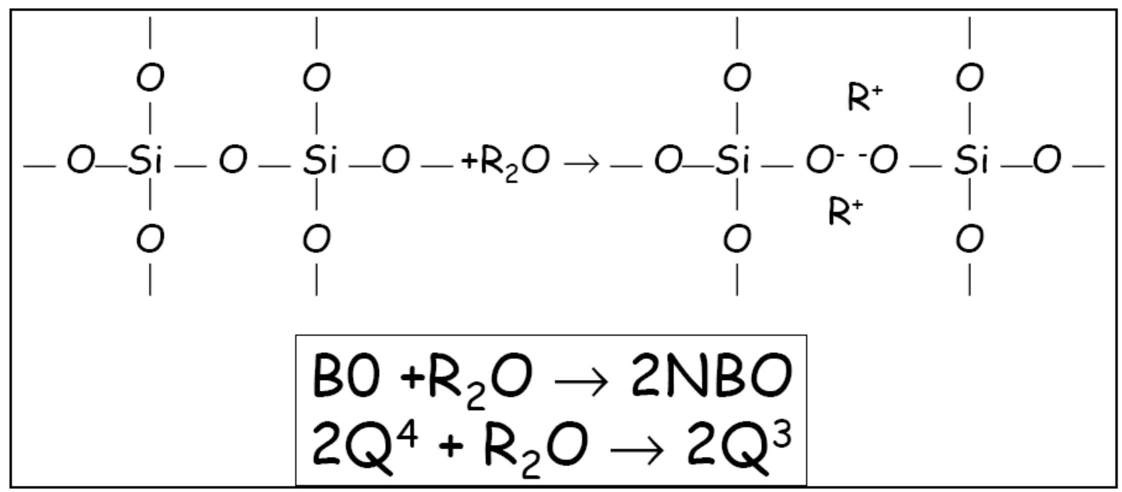
*BO = Bridging oxygen , NBO = Non-bridging oxygen

Structure of glass

Alkali silicate glass

- Every alkali ion creates one new NBO;
- Every alkali oxide 'molecule' creates two NBO's





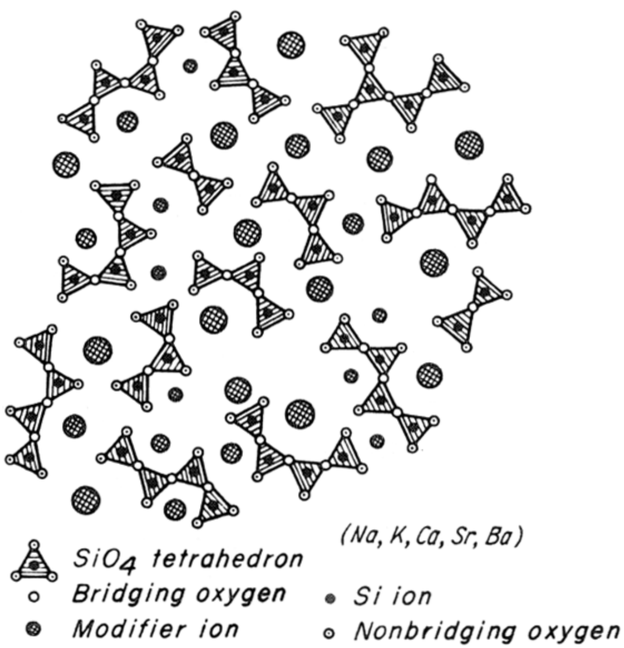
$$[O]_3Si\text{-}O\text{-}Si[O]_3 + Na_2O = [O]_3Si\text{-}O^{-}Na^{+} + Na^{+-}O\text{-}Si[O]_3$$

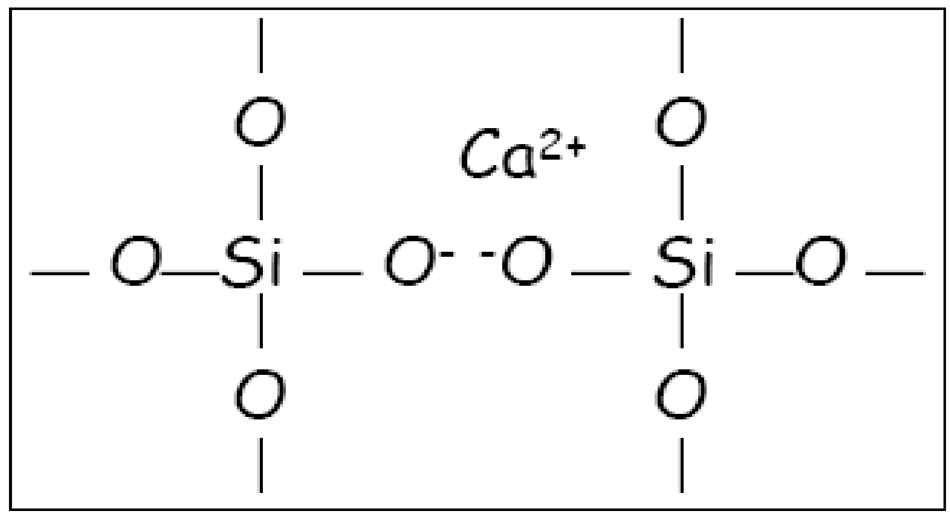
Note: adding alkalis increases ion density, 'filling in' the holes in the network

Structure of glass

Alkali-earth silicate glass

- When an alkaline earth ion containing oxide, such as CaO, is added to silica, the bivalent alkaline earth ion is attached to two NBOs





Structure of glass

What accounts for these properties changes?

-Effects on properties will depend on field strength (Z/r_c^2) of modifying cation

Increasing r_c?

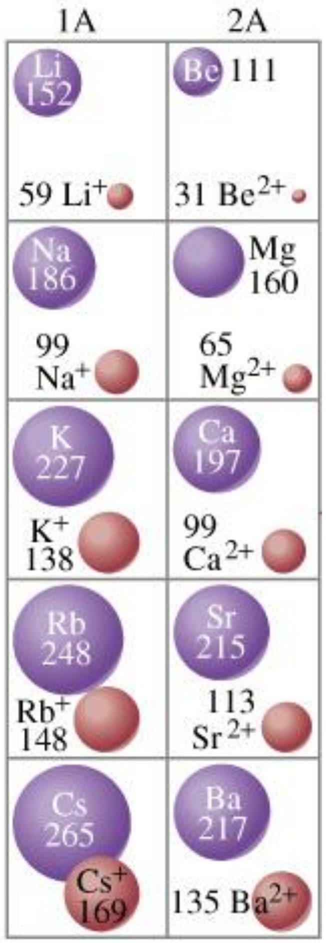
-Li^+-NBO stronger than Na^+-NBO stronger than K^+-NBO, Cs_2O is the better flux

- Mg^{2+}-NBO stronger than Li^+-NBO Mg-glasses are more refractory..

Note: Network connectivity for $25Na_2O\ 75SiO_2$ and $15Na_2O\ 10CaO\ 75SiO_2$ are the same

([O]/[Si] = 2.33, so same NBO/BO, same Q-distributions)

But, different properties (SLS more refractory, more durable).



Preparation of glass

Example 1

1.1 Glass composition : $65CaO\text{-}35Al_2O_3$

1.2 Molecular weight of components (in unit g/mol)

- CaO = 56.08 g/mol
- Al_2O_3 = 101.96 g/mol

Molecular weight of glass: $(0.65 \times 56.08) + (0.35 \times 101.96) = 72.14$ g/mol

1.3 Weight fraction of each component:

- CaO = $(0.65 \times 56.08) / 72.14 = 0.505$
- Al_2O_3 = $(0.35 \times 101.96) / 72.14 = 0.495$

1.4 For 30 grams of glass:

- CaO = $0.505 \times 30 = 15.15$ g
- Al_2O_3 = $0.495 \times 30 = 14.85$ g

Preparation of glass

Example 2

2.1 Glass composition : $20Na_2O$-$5Al_2O_3$-$75SiO_2$

2.2 Molecular weight of components (in unit g/mol)

- Na_2O = 56.08 g/mol
- Al_2O_3 = 101.96 g/mol
- SiO_2 = 60.09 g/mol

Molecular weight of glass: (0.20x61.95) + (0.05x101.96) + (0.75x60.09)
= 62.56 g/mol

2.3 Weight fraction of each component:

- Na_2O = (0.20x61.98) / 62.56 = 0.198
- Al_2O_3 = (0.05x101.96) / 62.56 = 0.0815
- SiO_2 = (0.75x60.09) / 62.56 = 0.720

2.4 For 20 grams of glass:

- Na_2O = 0.198x20 = 3.96 g
- Al_2O_3 = 0.0815x20 = 1.63 g
- SiO_2 = 0.720x20 = 14.40 g

Preparation of glass

Note: Na_2O is not stable in air

So use "**Na_2CO_3**", which yields Na_2O after decomposition. It is necessary to multiply the desired quantity of Na_2O by the "***gravimetric factor***" for Na_2CO_3 (1.71) to obtain the weight of Na_2CO_3 (3.96 g x 1.71 = 6.77 g) to be used to yield the desired 3.96 g of Na_2O

Note..

$$\mathbf{Na_2CO_3 \longrightarrow Na_2O + CO_2}$$

Na_2CO_3 ***A*** g has molecular weight = 105.9884 g/mol

Na_2O ***B*** g has molecular weight = 61.97894 g/mol

So we would found to the ***A*** = (105.9884 / 61.97894) x ***B***

= <u>1.71</u> ***B***

Gravimetric factor

Preparation of glass

Note..

$$2\ NH_4H_2PO_4 \rightarrow P_2O_5 + 3H_2O + 2NH_3$$

$NH_4H_2PO_4$ ***A*** g has molecular weight	= 115.0257 g/mol
$NH_4H_2PO_4$ ***A*** g has molecular weight	= 230.0514 g/mol
P_2O_5 ***B*** g has molecular weight	= 141.9446 g/mol
So we would found to the ***A***	= (230.0514/ 141.9446) x ***B***
	= <u>1.6208</u> ***B***

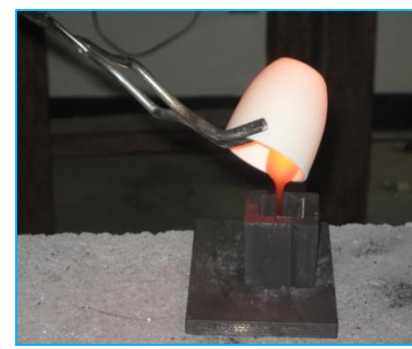
<u>Gravimetric factor</u>

Preparation of glass

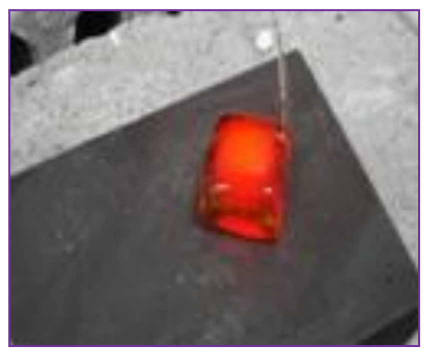
Electric Furnance (EF.)

Put alumina crucible in EF.

Melting XXX ^{o}C, 3 hr.



Poured into preheat stainless steel mould



Glass samples

Annealed at 500 ^{o}C, 3 hr.

Next week

Course Outine:

Week 2: Glass formation principle

- Zachariasan's random network theory
- Sun's single bond strength criterion
- Dietzel's field strength criterion