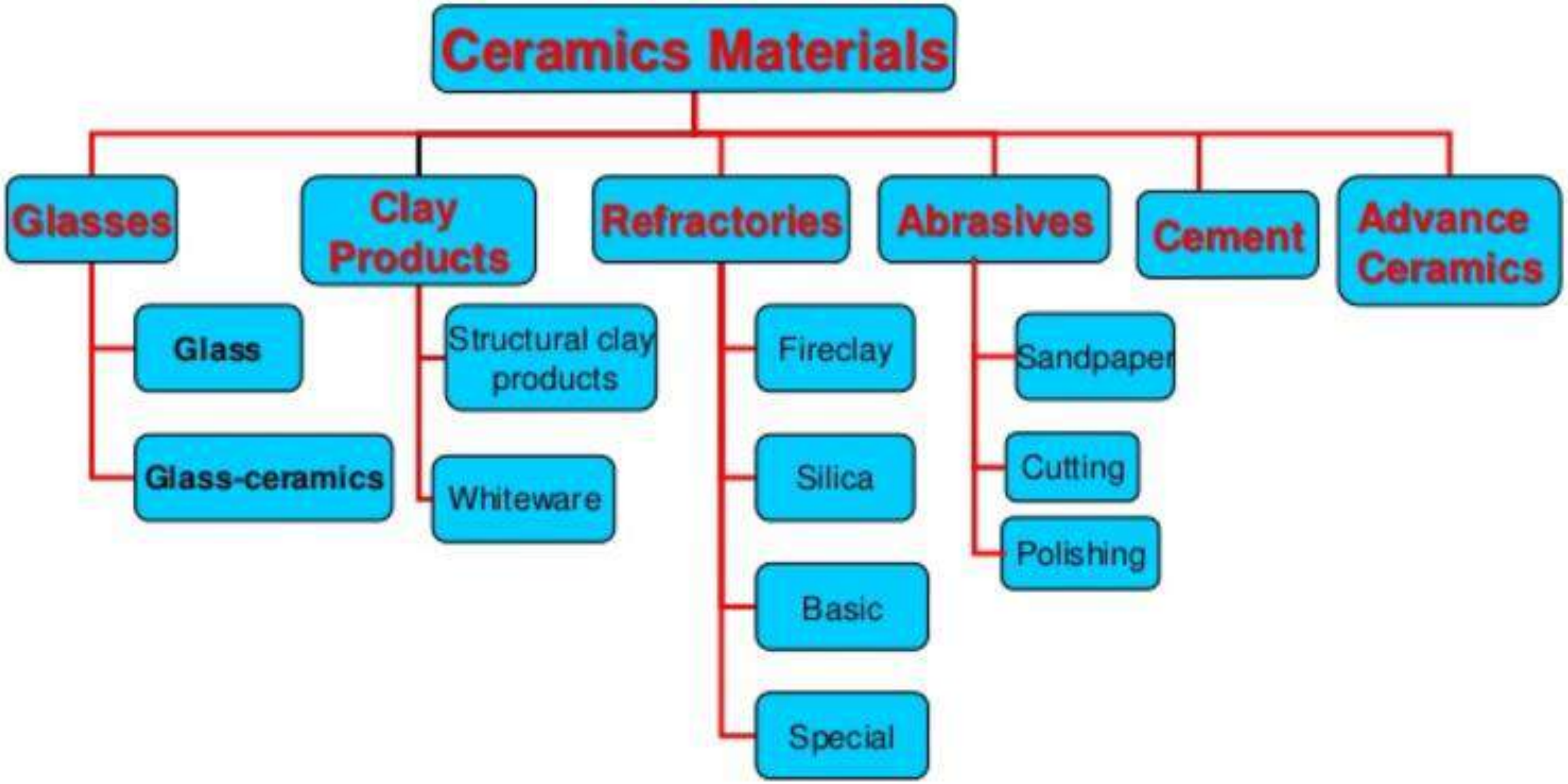
MME 3307
Glass and Glass ceramics

Part 1

Outline

- Glass Structure
- Glass properties
- Glass types
  - Soda lime glasses
  - Lead glasses
  - Heat-resistant/borosilicate glassess
  - High purity silica glasses
  - Specialty glass
- Glass manufacturing Process
- Glass forming
- Heat treating Glasses
  - Annealing glass
  - Tempering glass

Taxonomy of Ceramics



Glasses

- *A glass can be defined as an inorganic product which has cooled to rigid structure without crystallization.*
- Glass is hard material normally fragile and transparent common in our life.

❑ *Glass-ceramics* have an amorphous phase and one or more crystalline phases and are produced by a so called "*controlled crystallization*" in contrast to a spontaneous crystallization

❑ Glass-ceramics are mostly produced in two steps:

- ✓ First, a glass is formed by a glass manufacturing process.
- ✓ The glass is cooled down and is then reheated in a second step. *In this heat treatment the glass partly crystallizes*

❑ Two prime characteristics of glass are their optical transparency and the relative ease with which they may be fabricated.

Amorphous Ceramics (Glasses)

❑ Main ingredient is Silica (SiO_2)

❑ If cooled very slowly will form crystalline structure.

❑ If cooled more quickly will form amorphous structure consisting of disordered and linked chains of Silicon and Oxygen atoms.

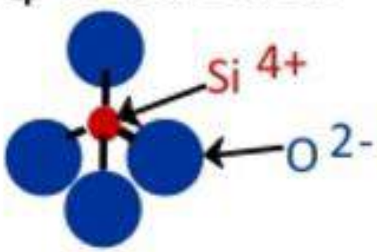
❑ This accounts for its transparency as it is the crystal boundaries that scatter the light, causing reflection.

❑ Glass can be tempered to increase its toughness and resistance to cracking.

Glass Structure

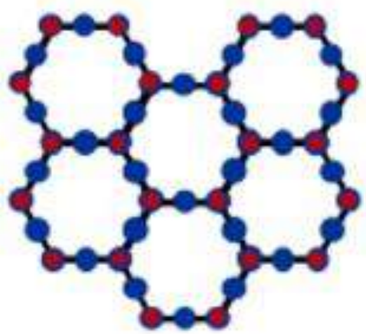
- Basic Unit:

SiO_4^{4-} tetrahedron



- Quartz is crystalline

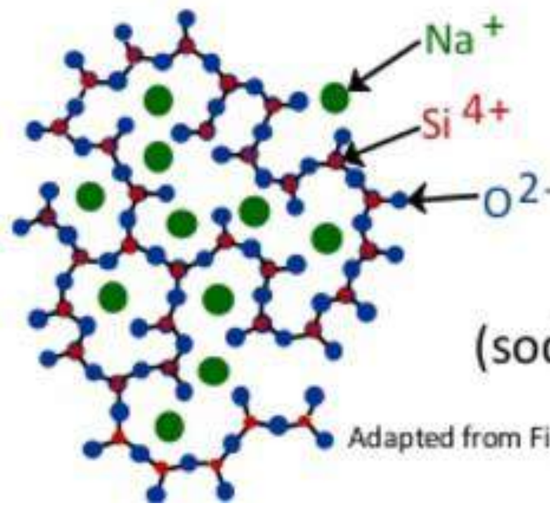
SiO_2:



- Glass is amorphous
- Amorphous structure

  occurs by adding impurities (Na^+, Mg^{2+}, Ca^{2+}, Al^{3+})
- Impurities:

  interfere with formation of crystalline structure.

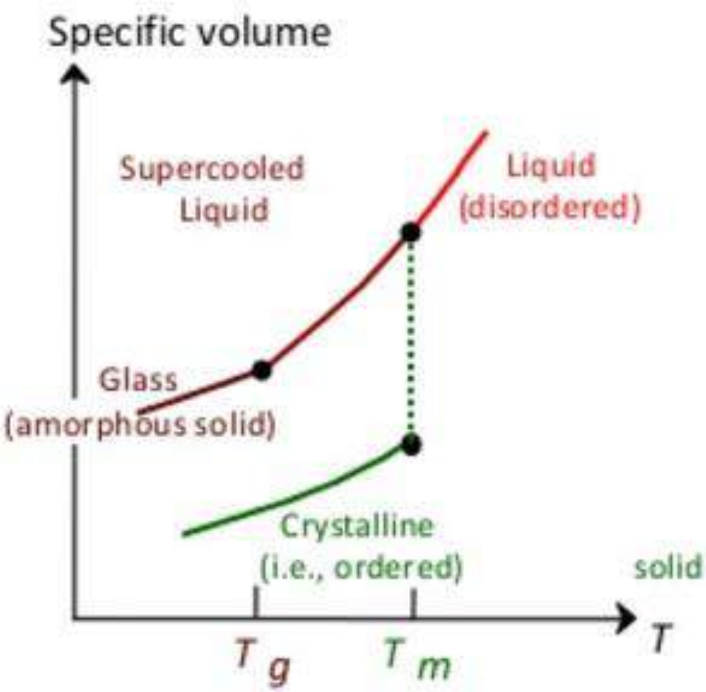


(soda glass)

Adapted from Fig. 12.11, *Callister, 7e*.

Glass Properties

❑ Specific volume ($1/\rho$) vs Temperature (T):



Adapted from Fig. 13.6, *Callister, 7e.*

❑ Crystalline materials:

➢ crystallize at melting temp, T_m

➢ have abrupt change in spec. vol. at T_m

• Glasses:

➢ do not crystallize

➢ change in slope in spec. vol. curve at glass transition temperature, T_g

-- transparent

- no crystals to scatter light

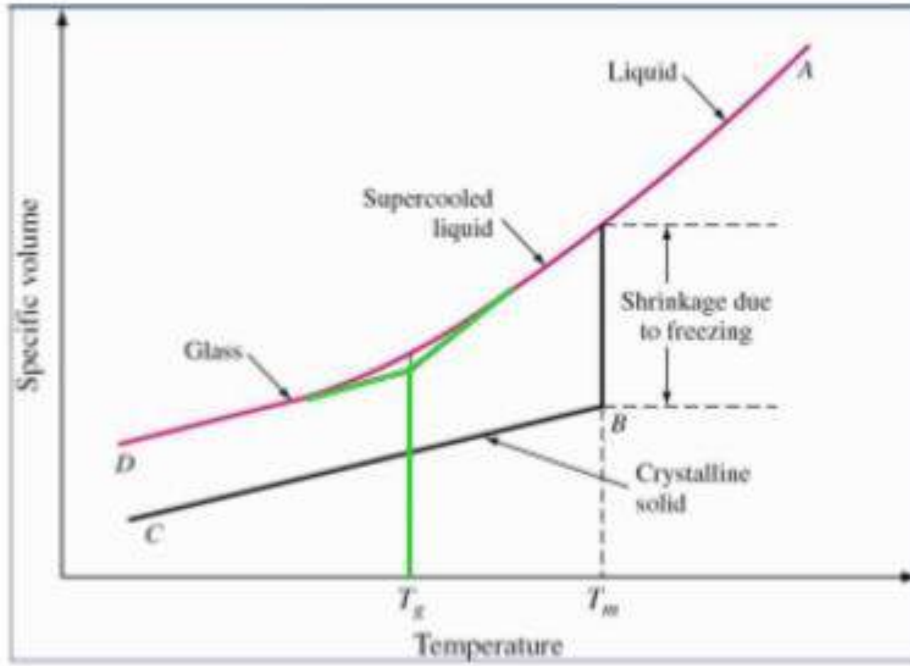
Glass transition temperature (T_g)

• Unlike solidified metal, a glass liquid does not crystallize but follow an ***AD*** path.

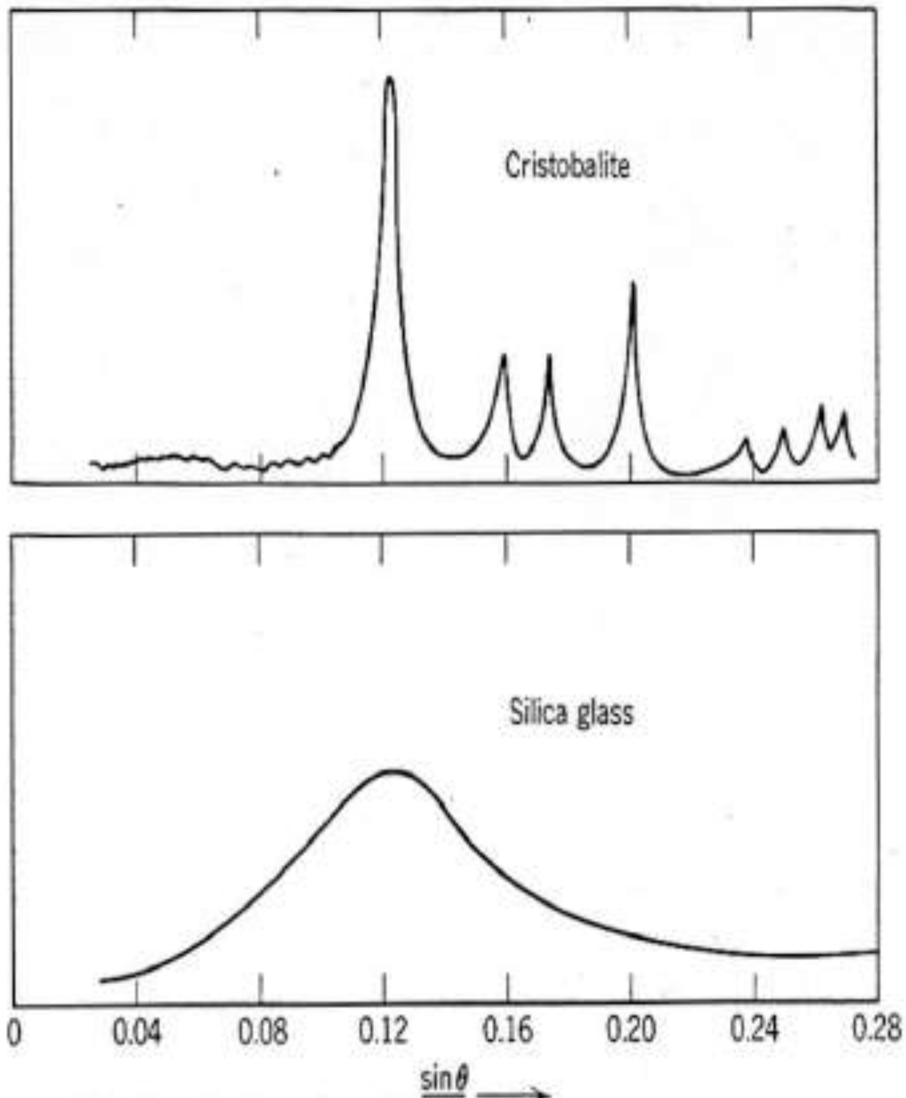
Temp (decrease)

Viscous → Plastic → Glassy

• The faster cooling rate, the higher values of T_g.



Solidification of crystalline and amorphous materials showing a change in specific volume



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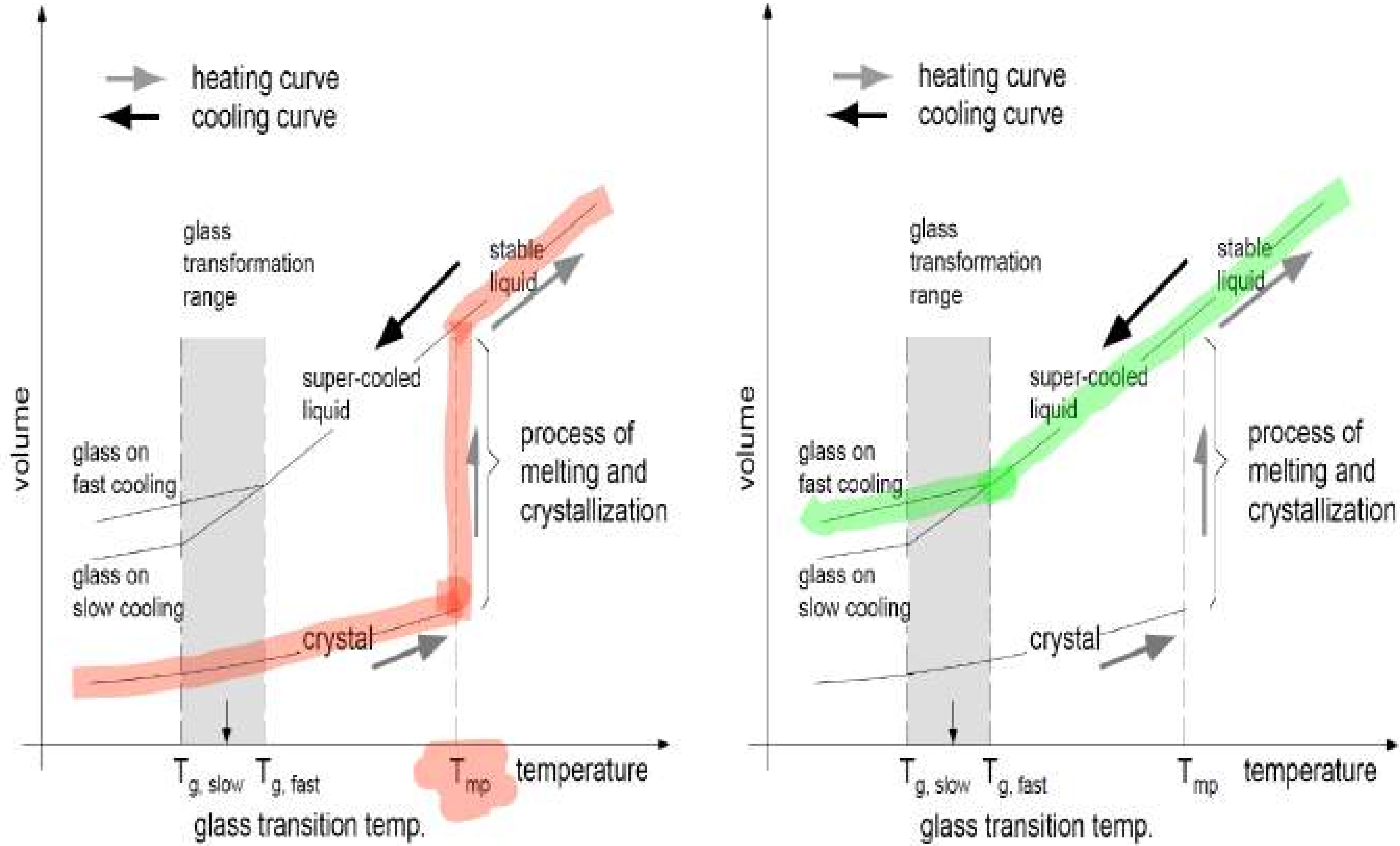

heating curve
cooling curve
glass
transformation
range
stable
liquid
super-cooled
liquid
process of
melting and
crystallization
glass on
fast cooling
glass on
slow cooling
crystal
volume
$T_{g,\ slow}$ $T_{g,\ fast}$
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temperature
glass transition temp.
heating curve
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T_{mp}
temperature
glass transition temp.

Viscous deformation of glasses

- Glass remains its viscous (supercooled) liquid above T_g.

Temp > T_g ↑ Viscosity ↓

- Viscous above T_g and viscosity decreases with increase in temperature.

$$\eta = \eta_o e^{+Q/RT}$$

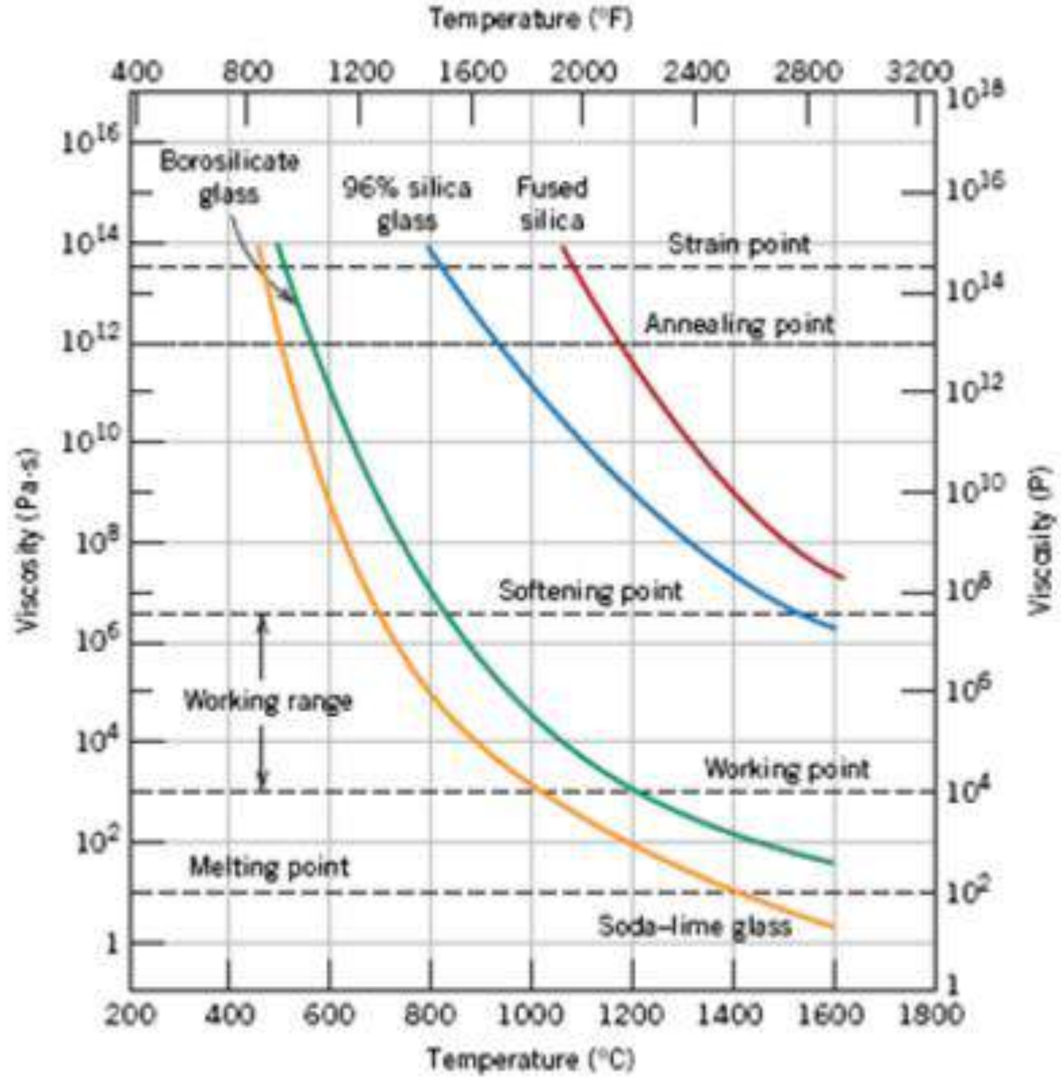
η = viscosity of the glass

η_o = pre-exponential constant

Q = molar activation energy for viscous flow

R = gas constant

T = absolute temperature

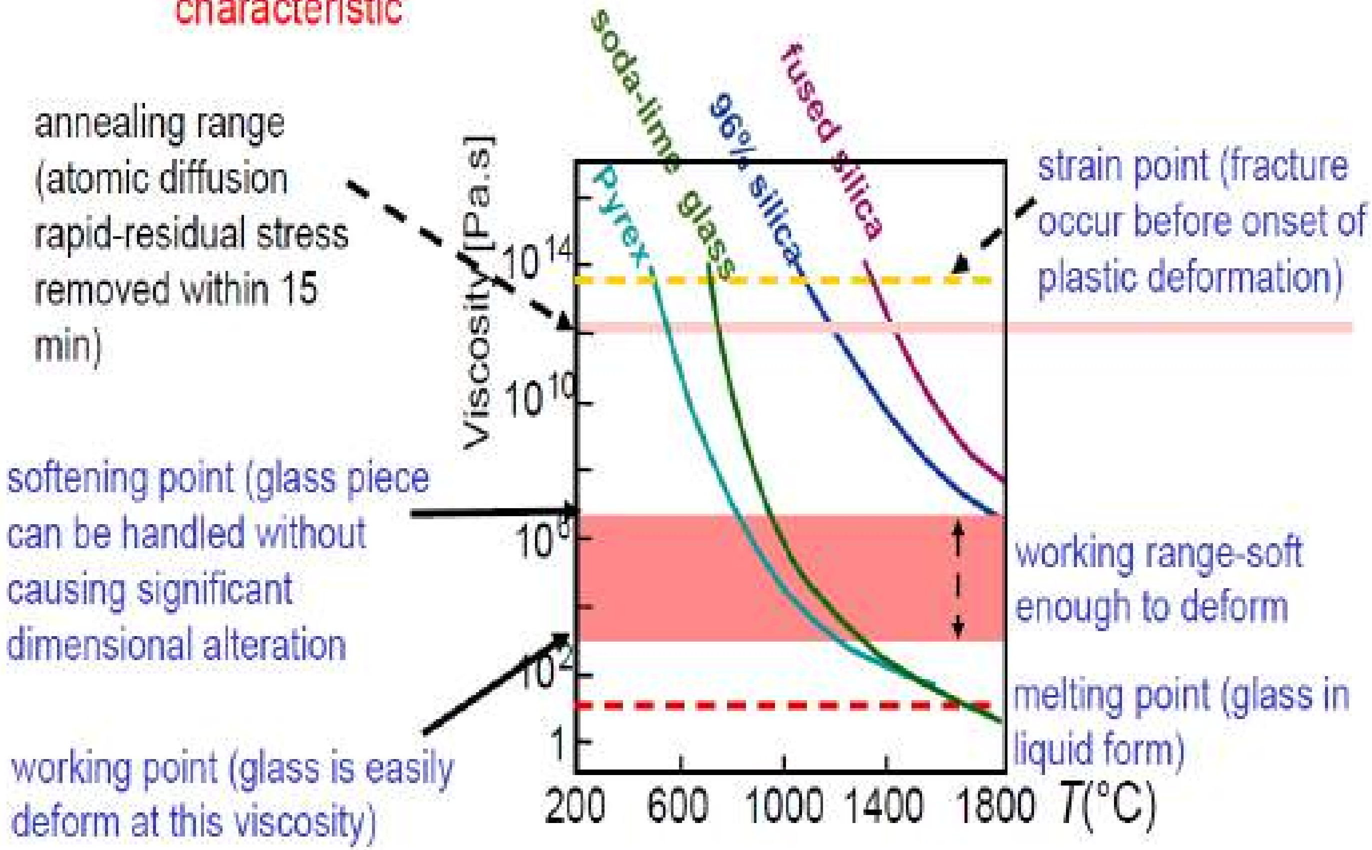


1. Working point: 10^3 PaS – glass fabrication can be carried out
2. Softening point: 10^7 PaS – glass flows under its own weight.
3. Annealing point: 10^{12} PaS – Internal stresses can be relieved..
4. Strain point: $10^{13.5}$ PaS – glass is rigid below this point.

Glass Properties: Viscosity vs. T and Impurities

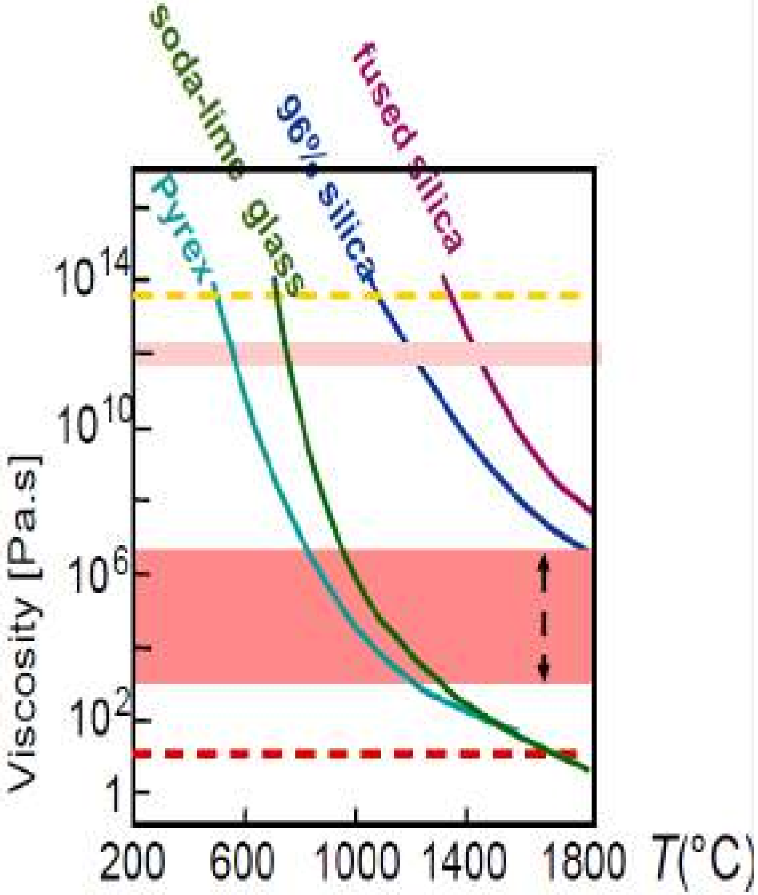
- Viscosity decreases with *T*

important factor in glass forming process is viscosity- temperature characteristic



Glass Viscosity vs. T and Impurities

- soda-lime glass: 70% SiO_2
  balance Na_2O (soda) & CaO (lime)
- borosilicate (Pyrex):
  13% B_2O_3, 3.5% Na_2O, 2.5% Al_2O_3
- Vycor: 96% SiO_2, 4% B_2O_3
- fused silica: > 99.5 wt% SiO_2



- Impurities lower *T* deform

working point: ($\eta \approx 10^5$ poise) temperature above which it is possible to *form* the glass, *i.e.*, press, draw, shape

softening point: ($\eta \approx 10^8$ poise) temperature above which glass *flows under its own weight*

annealing point: ($\eta \approx 10^{13}$ poise) temperature above which *residual stresses can be relieved within 15 min*

strain point: ($\eta \approx 10^{15}$ poise) temperature below which glass can be *rapidly cooled* without introducing internal stresses capable of fracture

1 Pa s = 10 poise; $\eta_{water} \approx 10^{-2}$ poise

Glass Types

Five common types of glass:

i) Soda-lime glasses

ii) Lead glasses

iii) Borosilicate or Heat-resistant glasses

iv) High-purity Silica glasses

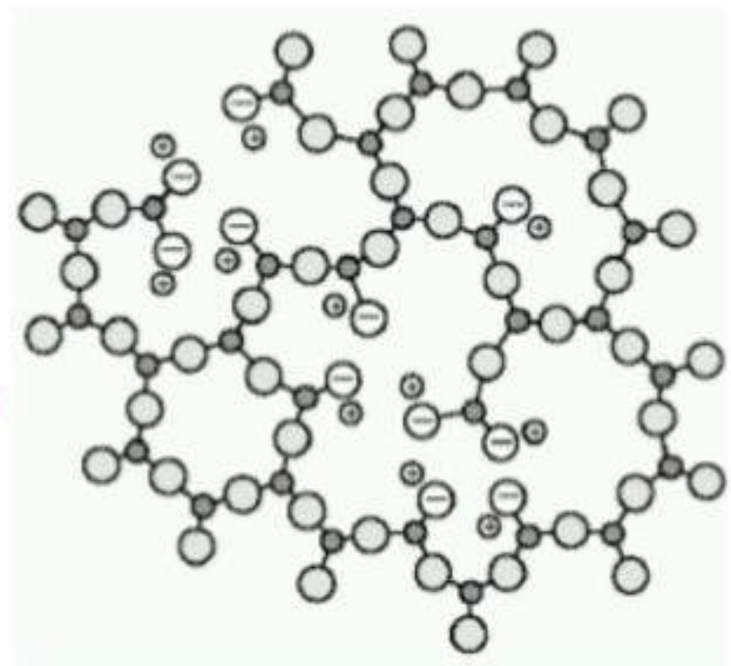
v) Speciality glasses

TABLE 14-6 ■ ***Compositions of typical glasses (in weight percent)***

Glass	SiO_2	Al_2O_3	CaO	Na_2O	B_2O_3	MgO	PbO	Others
Fused silica	99							
Vycor™	96				4			
Pyrex™	81	2		4	12			
Glass jars	74	1	5	15		4		
Window glass	72	1	10	14		2		
Plate glass/Float glass	73	1	13	13				
Light bulbs	74	1	5	16		4		
Fibers	54	14	16		10	4		
Thermometer	73	6		10	10			
Lead glass	67			6			17	10% K_2O
Optical flint	50			1			19	13% BaO, 8% K_2O, ZnO
Optical crown	70			8		10		2% BaO, 8% K_2O
E-glass fibers	55	15	20		10			
S-glass fibers	65	25				10		

i) Soda-Lime-Silica Glasses

- 65% sand; 15% soda; 10% lime
- In this glass component are:
  - ✓ 71 – 73% SiO_2
  - ✓ 12 – 14% Na_2O
  - ✓ 10 – 12% CaO
- Adding sodium oxide (soda) lowers melting point
- Adding calcium oxide (lime) makes it insoluble
- Sodium and calcium ions terminate the network and soften the glass
- **The Na_2O & CaO decrease the softening point of this glass from 1600°C to 730°C, So that soda lime glass is easier to form.**
- **An addition of 1 – 4% MgO is added to Soda lime glass to prevent cracks.**
- **In addition of 0.5 – 1.5% Al_2O_3 is used to Increase the durability**
- Soda-lime-silica glass is most commonly produced glass which accounts for ~95% of all the glass produced in the world.
- Soda-lime-silica glass expands much when heated
  - ✓ Breaks easily during heating or cooling



Uses

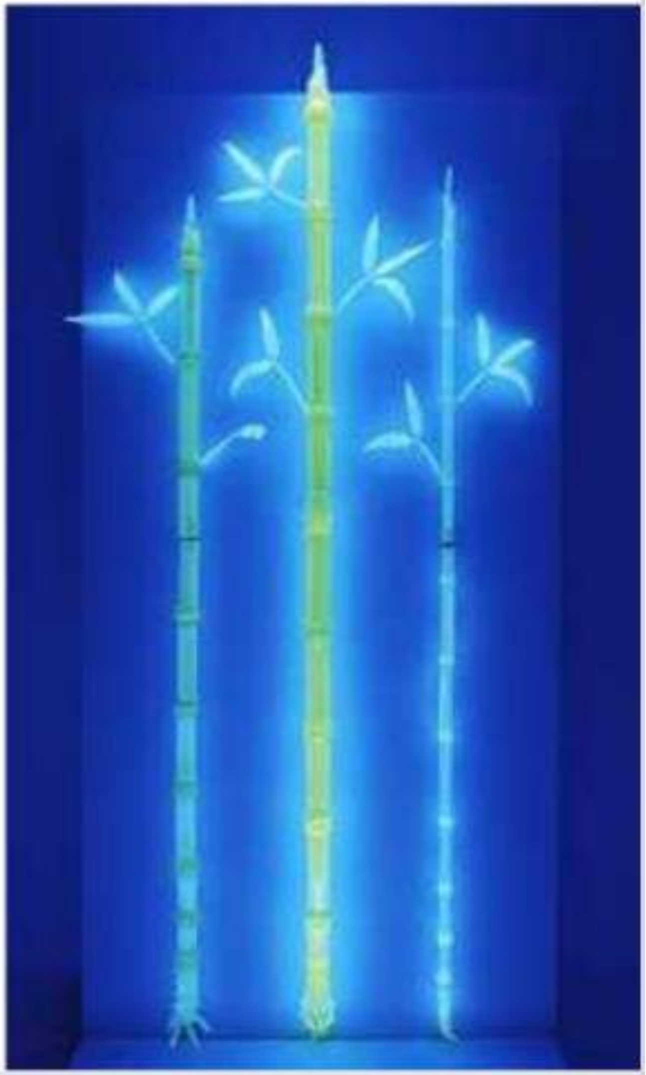
- Soda lime glass is used for flat glass, containers, lightening products.
- It is used where chemical durability and heat resistant are not needed

ii) Lead Glasses

- Lime and soda replaced with lead oxide (PbO)
- Contains lead oxide (PbO) to improve refractive index
- High refractive index- clarity sparkle
- Softer –cut and engrave
- Good electrical resistance - electronics

iii) Heat-resistant (or Borosilicate) Glasses

- Contains Boron oxide, known as ***Pyrex.***
- Boron-oxide-silica glass expands less
  - ✓ Tolerates heating or cooling reasonably well
- Pyrex and Kimax are borosilicate glasses
- Boron oxide replaces lime and most of soda – low thermal expansion coefficient
- Al_2O_3 - B_2O_3 – aluminosilicate glass with even better heat resistance



iv) High-purity Silica Glasses

- Highest quality – most durable
- 3 processes – melting pure SiO_2; making 96% silica and flame hydrolysis
- ***Pure SiO_2*** – pure silica melted @ 1900 °C under vacuum
- ***96%*** - Vycor process – borosilicate glass heated to grow crystalline sodium borate channels – extracted hot HNO_3 – leaving 96% pure silica after heat reduction @ 1200 °C
- ***flame hydrolysis*** – $SiCl_4$ in CH_4 / O flame (1500°C, produces high-surface silica soot thermally sintered to pure silica at 1723 °C)

$$2H_2O + SiCl_4 \xrightarrow{\text{Flame}} SiO_2 + 4HCl$$

v) Specialty Glasses

- ***Coloured glass:***
  - MnO_2 – violet,
  - CoO – blue,
  - Cr_2O_3 - green
- ***Opal glass:***
  - white opaque or translucent glassware
  - colour due to scattering of light from small particle
  - usually NaF/CaF crystals
  - nucleating after a cooling and reheating process
- ***Frosted glass:***
  - satiny look when exposed to HF

$$4HF + SiO_2 \rightarrow SiF_4 \uparrow + 2H_2O$$

v) Speciality (Cont.)

- ***Coated glass:***
  - ✓ unique properties
  - ✓ metal / metal oxides Ag+ + RA $\rightarrow$ Ag$\downarrow$ mirror
  - ✓ electrically conducting with SnO_2 coating (thermal $SnCl_4$ hydrolysis)
- ***Photosensitive glass:–***
  - ✓ glass that changes colour upon exposure to light
  - ✓ ***Phototropic:***
    - ❖ darkens upon exposure to light and returns to original clear sate afterwards.
    - ❖ AgCl/AgBr

$$\underset{\text{colorless}}{Ag^+ X^-} \underset{\text{dark}}{\overset{\text{light}}{\longleftrightarrow}} \underset{\text{Blue-grey}}{Ag + X}$$

▪**Non-silicate glasses** are becoming increasingly important for special optical purposes,

- ✓ **for example in the use of glasses prepared from CaF_2, AlF_3 and P_2O_5 for infrared optics or the use of fluoride glasses for *optical fibres***

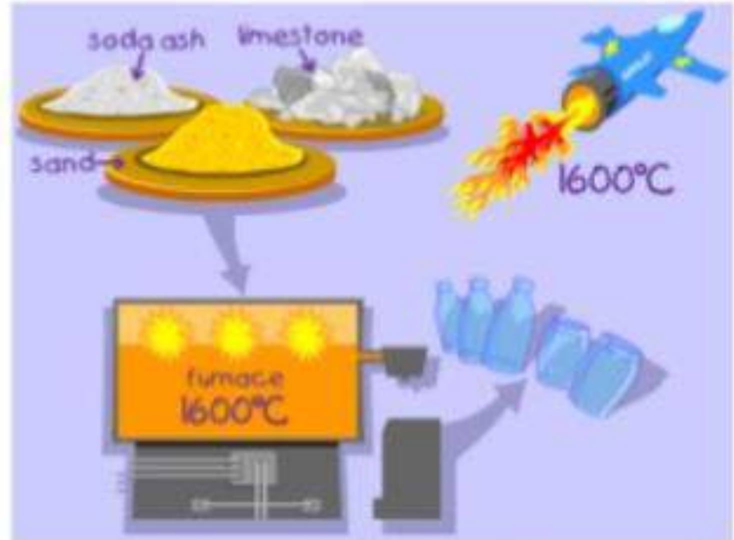
Glass composition

- ***Silica glass***
  No radiation damage
- ***Soda-lime glass***
  Reduced T_m ~ 730 °C
- ***Borosilicate glass (Pyrex glass)***
  Low thermal expansion
- ***Lead glass***
  Shielding from high energy radiation

Type	Composition, w/o								Properties or uses
	SiO_2	Na_2O	K_2O	CaO	MgO	B_2O_3	Al_2O_3	Other	
Soda-lime	72	14		9	4		1		Window glass
Silica glass (fused quartz)	99.5+								High-temperature applications; low coefficient of expansion
96% silica glass	96.3	<0.2	<0.2			2.9	0.4		Comparable to fused quartz
Borosilicate	80.5	3.8	0.5			12.9	2.2		Resistant to heat and to chemicals
Light flint optical	54	1	8					37PbO	High index of refraction
Surface-strengthened glass	55	16	2	2		2	19	$4TiO_2$	Cookware
Glass-ceramic	56				15		20	$9TiO_2$	Radomes

Glass Manufacturing Process

1. Silica sand, limestone, soda ash and cullet (recycled glass or broken glass) are keep dry and cool in a batcher house in silos or compartments
2. Mixing and weighting into proper proportion:
   - ✓ **Sand** (SiO_2), Quartz, or Silica sand 72%
   - ✓ **Flux** → to lower T – e.g. ***Soda or*** Soda Ash ($NaHCO_3$) 17%; (1700 – 900°C)
   - ✓ **Stabilizing agent** → to mitigate water solubility of the glass formed – e.g. CaO normally added as Limestone {Lime 5%}



www.glassforever.co.uk/howisglassmade/

Why So Much SiO_2 in Glass?

- Because SiO_2 is the best *glass former* :
  - Silica is the main component in glass products, usually comprising 50% to 75% of total chemistry.
  - It naturally transforms into a glassy state upon cooling from the liquid, whereas most ceramics crystallize upon solidification.

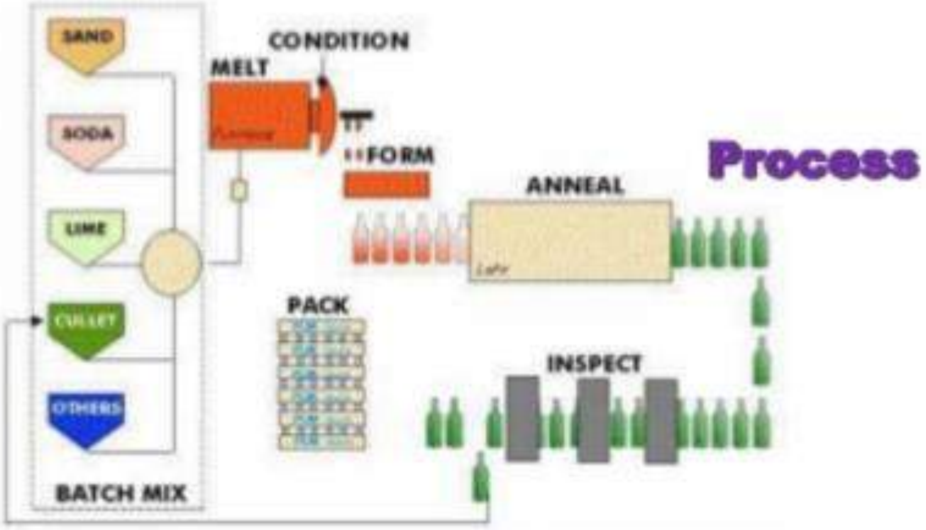
Other Ingredients in Glass

- Sodium oxide (Na_2O), calcium oxide (CaO), aluminum oxide (Al_2O_3), magnesium oxide (MgO), potassium oxide (K_2O), lead oxide (PbO), and boron oxide (B_2O_3)
- Functions:
  - ✓ Act as flux (promoting fusion) during heating
  - ✓ Increase fluidity in molten glass for processing
  - ✓ Improve chemical resistance against attack by acids, basic substances, or water
  - ✓ Add color to the glass
  - ✓ Alter index of refraction for optical applications

Glass Manufacturing Process (Cont.)

3. Send to furnaces in hoppers:
   - operated by natural gas
   - heat the mixture at 1300-1600°C into soften or molten state
4. ***Molding*** (or ***Casting***)*:* molten glass flows to forming machine to mold into desire shapes
5. ***Annealing lehrs :*** reheating the glass in an oven
   - to ensure even cooling of glass for strengthening of the products
6. ***Cooling process:*** Cool for 30 min to an hour for safe to handle.
7. ***Glass products*** are then decorated, inspected again and finally packaged and shipped to our customers.

Glass Furnace Cooling Systems

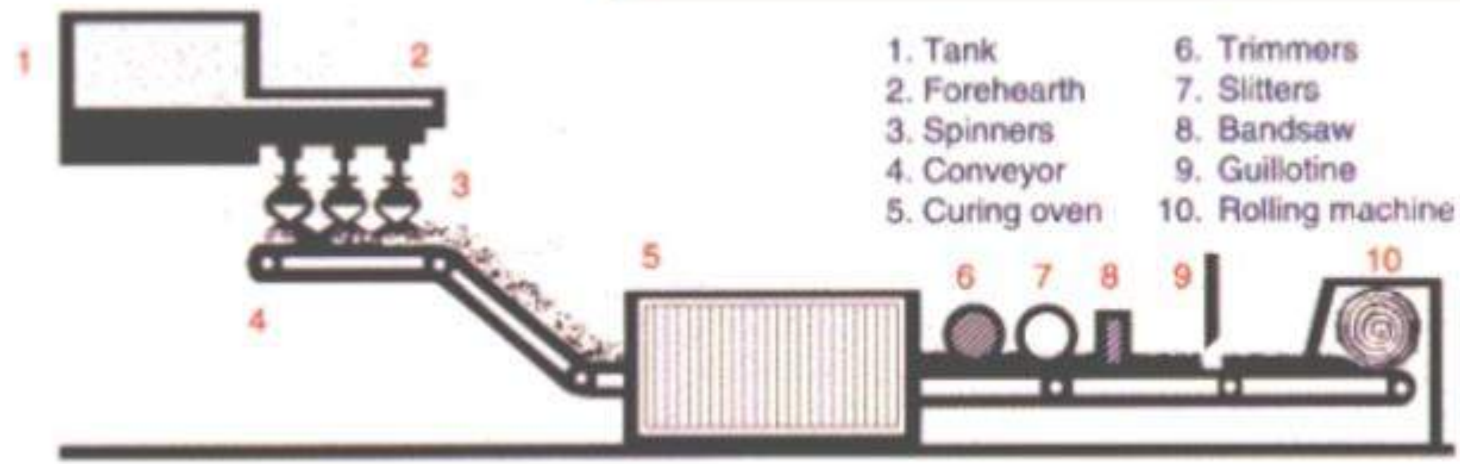


Glass Forming

1) ***Casting :*** molding
2) ***Pressing:*** pressing second mold into molten glass
3) ***Core-forming:*** clay core dipped into molten mass
4) ***Fusing :*** fusing glass rods together around a mold
5) ***Blowing:*** blowing air into a glob

Flat glass – floating / rolling

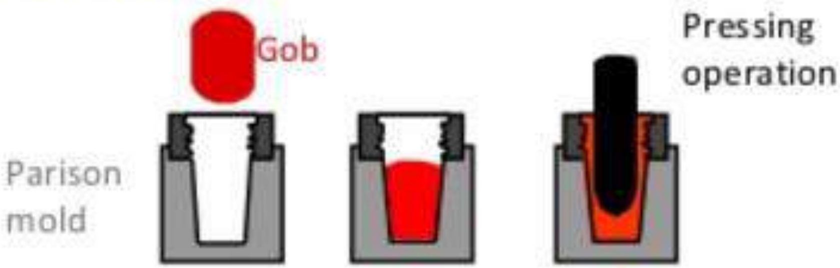
Glass fibre – continuous strands and Crown process for glass wool



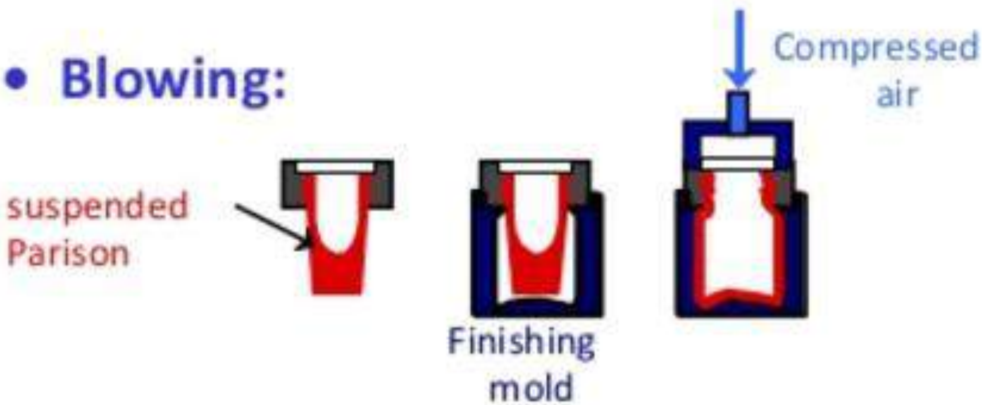
Glass Fabrication Methods

GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- **Pressing:**



- **Blowing:**

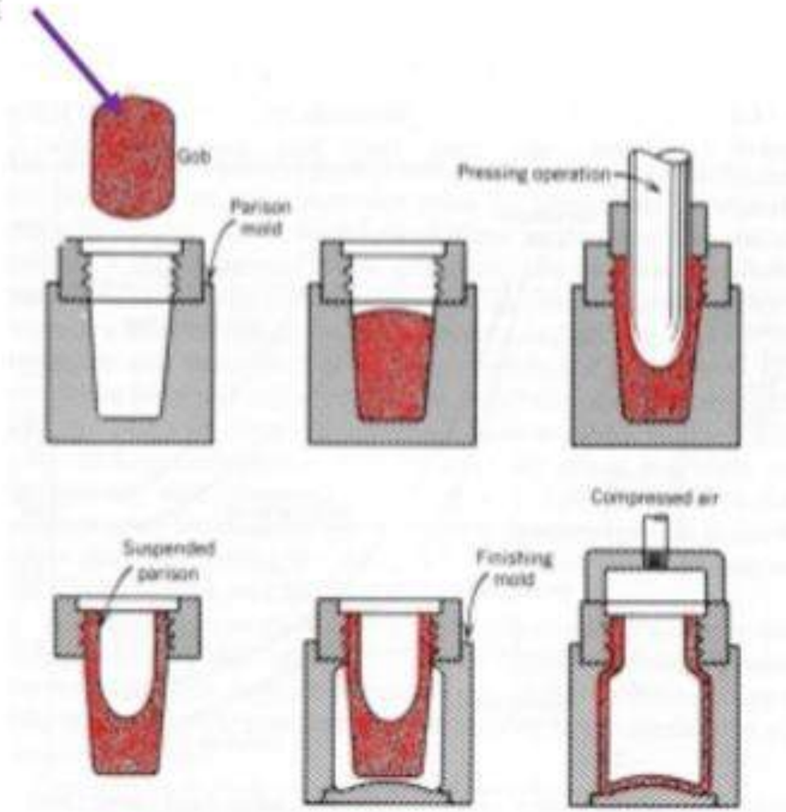


plates, dishes, cheap glasses
-mold is steel with graphite lining

- Fiber drawing:

Blow Molding

Softened glass

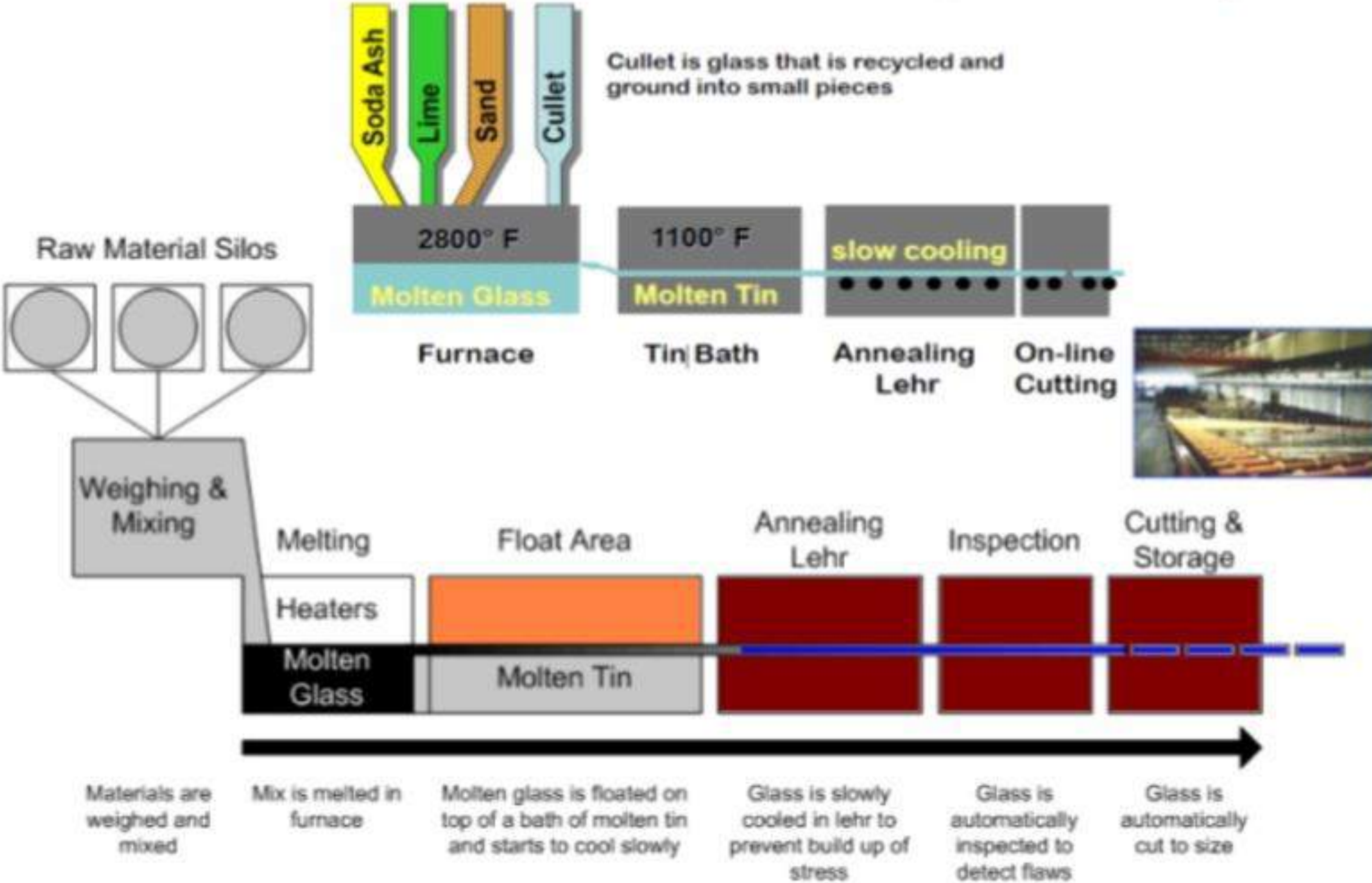


Pressed Glass Processing

Softened glass

Float Glass: The Process

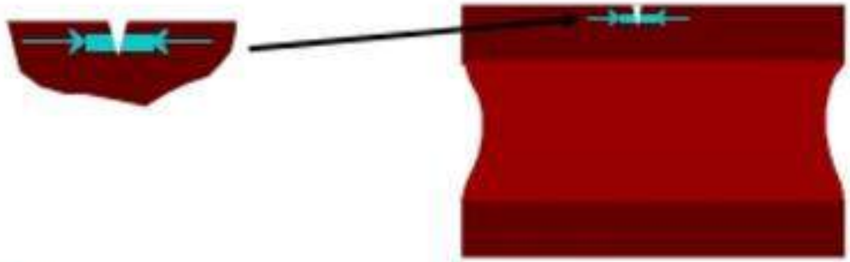
Modern Plate/Sheet Glass making:



Heat Treating Glass

- Annealing:
  - ✓ removes internal stress caused by uneven cooling.
- Tempering:
  - ✓ puts surface of glass part into compression
  - ✓ suppresses growth of cracks from surface scratches.
  - ✓ sequence:

➤ Result: surface crack growth is suppressed.

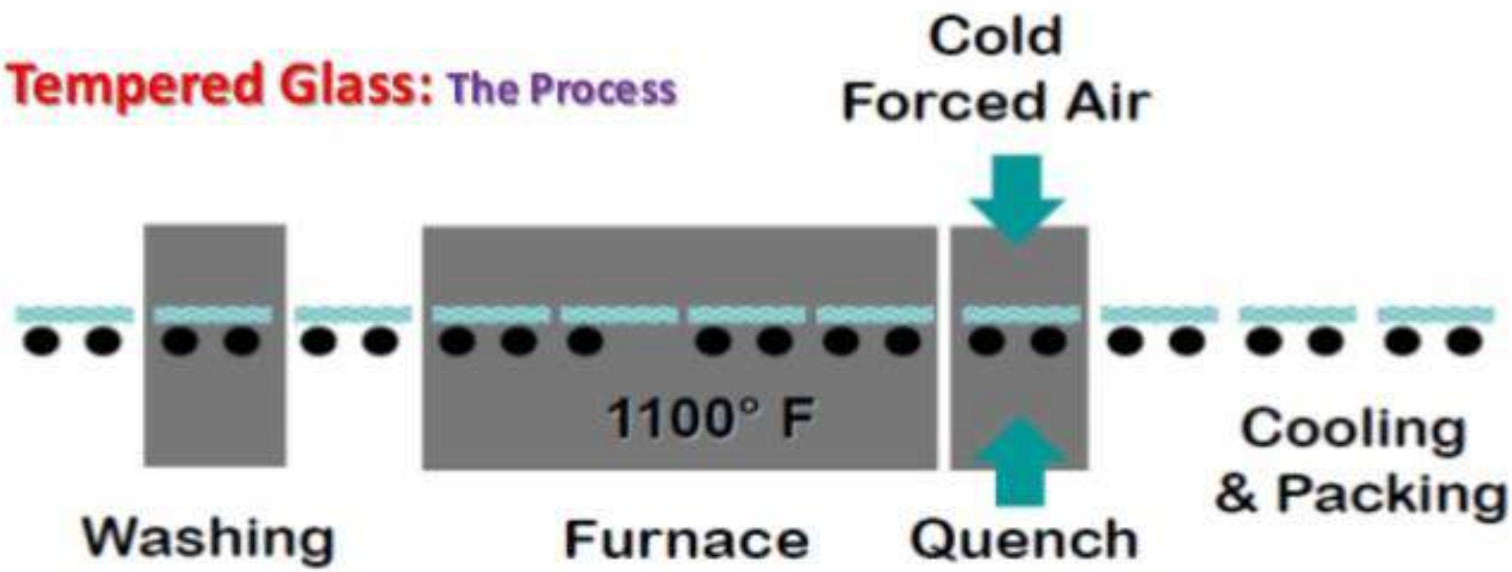


a) Annealing Glass

- ***Annealing*** is a process of slowly cooling glass to relieve internal stresses after it was formed.
- The process may be carried out in a temperature-controlled kiln known as **a Leh**r.
- Annealing glass is critical to its durability.
- Removes internal stress caused by uneven cooling.
- Glass which has not been annealed is liable to crack or shatter when subjected to a relatively small temperature change or mechanical shock.
- If glass is not annealed, it will retain many of the thermal stresses caused by quenching and significantly decrease the overall strength of the glass.

b) Tempered Glass

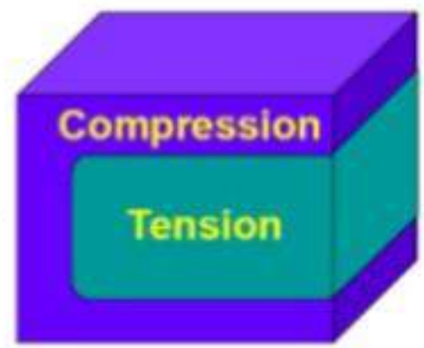
- The tempering process consists of the following steps:
    1) First the glass is washed and then heated.
    2) In order to temper glass, it must reach 1100°F (the softening point for glass.)
    3) The glass is then cooled with cold air. Quenching with forced cold air sets up the tension and compression zones.
    4) The tempered glass continues down the rollers to cool more and be packed for shipping. Glass to be tempered must be cut to size before the tempering step.
- A flow chart in the next slide provides a summary of the tempering process.



b) Tempered Glass (Cont.)

- Tempering glass:
  - ✓ Heat glass to softening point
  - ✓ Cool outside of glass quickly
  - ✓ Outside stiffens while inside is still hot
  - ✓ Shrinking inside compresses outside
  - ✓ Compressed outside stretches inside
- Resists fractures because surface is compressed
- Crumbles when cracked because inside is tense

- Glass expands when heated
- Quenching "freezes" this expansion on the outside
- Center cools more slowly, and contracts. Sets up tension and compression zones.
- Tempered Glass is required for door products and some windows installed near doors. If tempering is done improperly then distortion can result.
- ***Tempered glass is stronger than annealed glass.*** If annealed glass (raw float) has a strength factor of "1", tempered glass would be "4".



What is the difference between (regular) annealed glass and tempered glass?

Annealed (regular) Glass	Tempered Glass
• Advantages: ✓ Cost • Limitations: ✓ Breaks in sharp pieces ✓ Not as strong as Tempered Glass ✓ Size limitations	• Advantages: ✓ 4 times the stronger than annealed ✓ Breaks into small, harmless pieces. ✓ Qualifies as Safety Glazing • Limitations: ✓ Must be cut to size before tempering ✓ Optical distortion (roller wave, strain pattern)

Examples of today's glass products:

- Containers (jars and bottles)
- Flat glass (windows, vehicle glazing, mirrors, etc.)
- Lighting glass (fluorescent tubes, light bulbs, etc.)
- Tableware (drinking glasses, bowls, lead crystal, etc.)
- Laboratory equipments (test tubes, cylinders, measuring flasks, etc.)
- TV tubes and screens
- Decorative glass
- Fiberglass
- Optical glass
- Vacuum flasks

Class Assignment

1. Cite the two common characteristic of glasses.
2. What happen when molten SiO_2 cooled to form glass?
3. Why glass behave as brittle at room temperature ? What happen to the glass at high temperature?
4. Differentiate between anneal and tempering glass.

2 common characteristics glasses :

1) Do not have long range order (LRO) (short range atomic order –brittle)
   - no regularity in the arrangements of its molecular

2) Exhibit a time-dependant behaviour known as glass transition phenomenon
   - occurs over temperature range called the glass transition temperature.
   - as inorganic melt cooled to solid without recrystallization (amorphous solid)

"glass can be defined as an amorphous solid completely lacking in long range, periodic atomic structure and exhibiting a region of glass transformation behaviour ".