Doctoral Prog am in Microsystems and icroelectronics
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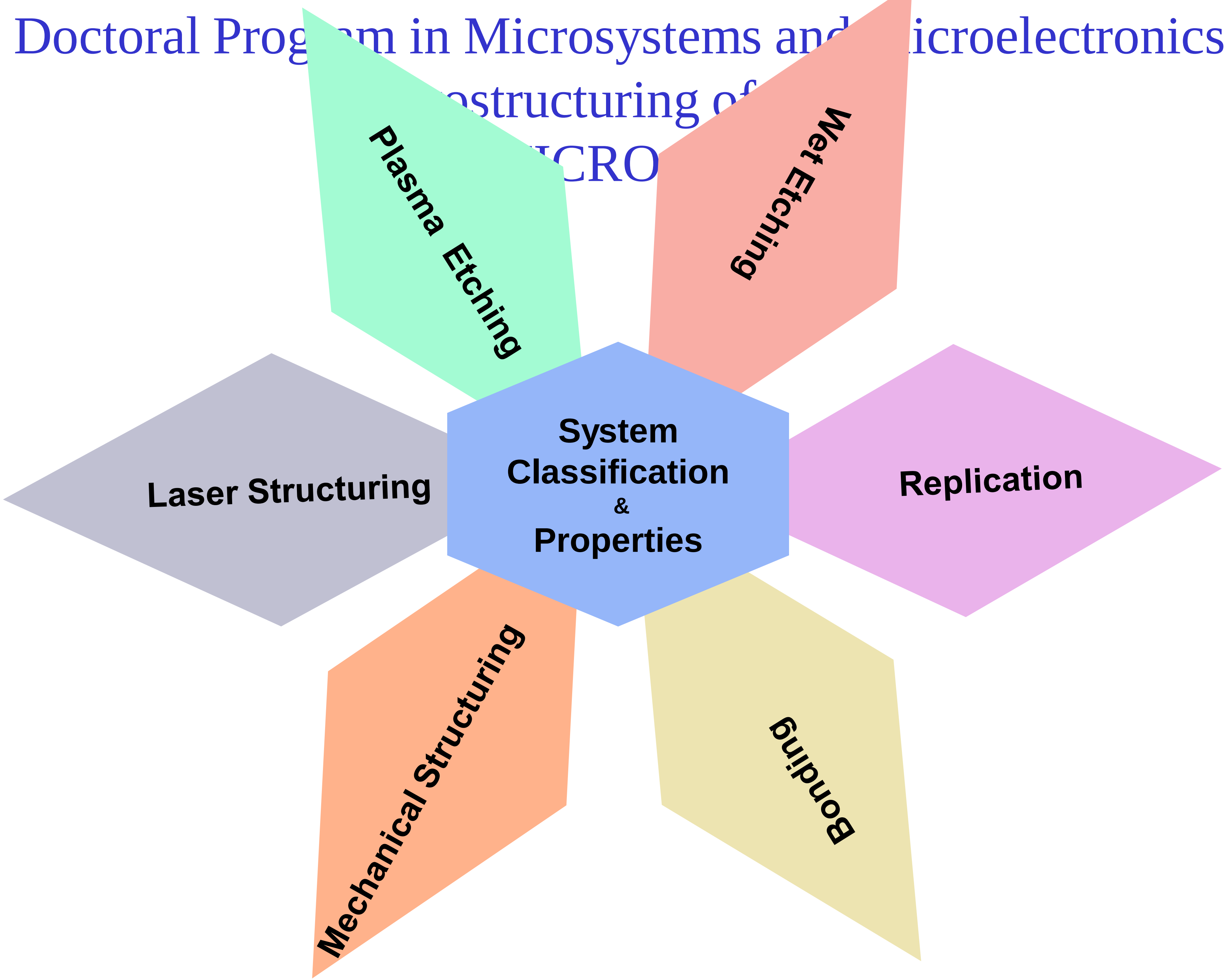

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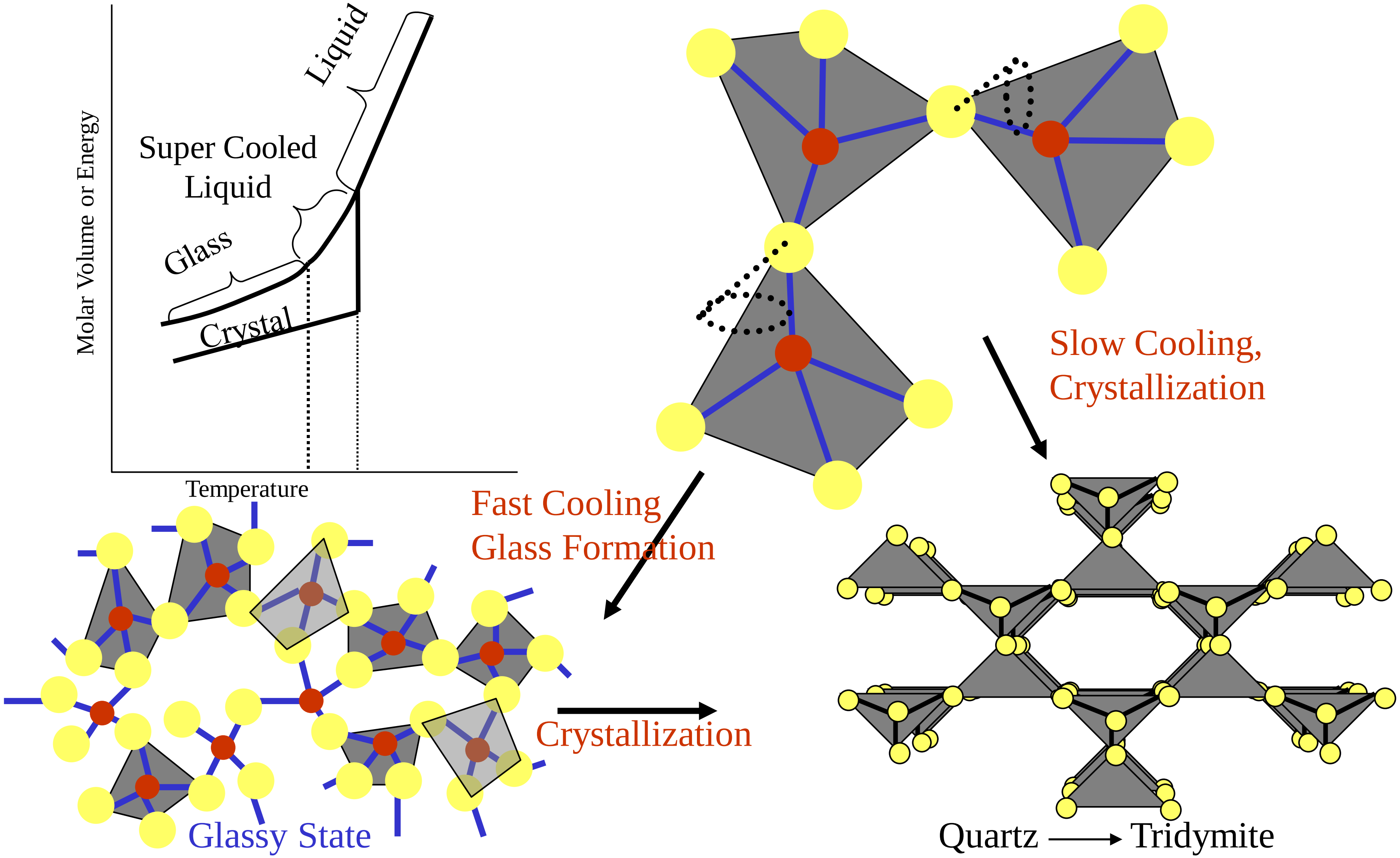
Glass State – SiO_2



Glass : An Important Material

- Mechanically Strong
- Hard :- surface resists scratches and abrasions
- Chemical corrosion-resistance
- Thermal Shock-resistance
- Heat Absorbent – retain heat rather than conduct it
- Electrical Insulating : resist current, stores electricity
- OPTICAL
    - Reflects
    - Refrects – Bends
    - Transmits
    - Absorbs

Glass : Easier for Microfabrication

- Chemical Structuring :- Wet & Dry Etching
- Mechanical Structuring :- Powder Blasting
- Replication :- Hot embossing & Solution chemistry
- Photolithography, UV

Glassy Systems

* Composition
- Oxide (Silicate)
- Chalcogenide
- Metallic
- Carbon

* Preparatory Methods
- ❖ Batch Melt
- ❖ CVD
- ❖ Sol-Gel

Glass - Definition

1949 ASTM

"Glass is a an inorganic product of fusion which has cooled to a rigid condition without crystallization"

Features of the Glassy State

Glass is a *non-crystalline* material that posseses no long range atomic order and, upon heating, gradually softens to the molten state

•Non-Crystalline structure
•Glass transformation behaviour

Oxide Glasses (Vitreous Silica)

- **Vitreous Silica - SiO_2**
  - Composition: SiO_2
  - Preparation: Higher melting point forces non-crucible melting techniques

    Chemical vapor deposition (CVD)

    $SiCl_4(g) + O_2(G) \quad SiO_2(s) + 2Cl_2(g)$

    SiO_2 solid soot is consolidated, sintered at elevated temperatures,

  Properties: Softening point ~1,200°C,

  Working range ~1,000°C

  Melting point, c-SiO_2 1,710°C

  Colorless, 165 nm (UV) to ~3000 nm (IR)

  Low Thermal expansion ~0.5 PPM/°C

  (Typical values ~ 10-100 PPM/°C)

Uses: Low expansion chemically resistant tubing

Light bulbs (UV transparency & thermal resistance is necessary)

Ultra-low loss telecommunication optical fiber

Low expansion mirrors and mirror blanks

Oxide Glasses (Soda - Lime - Silicate Glass)

- **Soda - Lime - Silicate Glass**
  - Typical Composition: 10-15 Na_2O + 5-15 CaO + 50-70 SiO_2
  - Preparation: Batch melting , $CaCO_3$(Limestone) + Na_2CO_3(soda ash + SiO_2(silica sand) @ ~ 1,300 1,500°C
  - Properties: Softening point ~500 - 600°C

    Colorless ~200 nm to ~3,000 nm

    Higher expansion 10 PPM/°C
  - Uses: The most common glass,

    Windows, bottles, containers, fibers, mirrors, lenses, tableware, light bulbs, etc.

Oxide Glasses (Borosilicate glass)

- **Borosilicate Glass - Pyrex**
  - Typical Composition: $80SiO_2 + \sim 10B_2O_3 + \sim 2Al_2O_3 + \sim 5Na_2O$
  - Preparation: Batch and continuous melting

    H_3BO_3 (Boric acid) + Na_2CO_3 (Soda ash) + SiO_2 (silica sand) + Al_2O_3 (alumina) $Na_2B_4O_7 \cdot 10H_2O$ (borax) + Al_2O_3 +SiO_2
  - Properties: Low expansion, 3-5 PPM/^oC

    Softening point ~ 700 - 800^oC

    High chemical durability
  - Uses: Chemical laboratory ware, cooking ware, high wear lenses such as automobile lenses

Oxide Glasses (E- or S-Glass)

- **Aluminosilicate Glass - (E- or S-Glass)**
  - Typical Compositions: $14\text{-}25Al_2O_3 + 0 - 10\ B_2O_3 + 15\ CaO$ or $MgO + 1\text{-}2\ (Na_2O, K_2O) + 50 - 60SiO_2$
  - Preparation: Batch melting, alumina, borax, soda ash, potash, limestone, magnesia, dolomite
  - Uses: high strength fibers, refractory glass application, chemically resistant glass, UV transparent light bulbs

Oxide Glasses (Crystal Glass)

- **Lead "Crystal" Glass**
  - Typical Compositions: 15 - 30 PbO + ~ 70 SiO_2 + ~ 5 Na_2O, K_2O
  - Preparation: Batch melting (PbO + soda ash or potash and silica sand)
  - Uses: Stemware, fine lead glass, art glass
  - Properties:
    - Low softening point, ~300 to 500°C
    - High expansion coefficient ~ 10 to 30 PPM/°C
    - High index of refraction 1.8 to 2 (1.5 window glass)
    - 300 to 3000 nm transparency
    - High density, 3 to 5 g/ml
    - High electrical resistivity

Non-Oxide Glasses

Glasses based upon glass forming anions other than oxygen

- Chalcogenide glasses – S, Se, Te-based
- Metallic glasses
- Glassy Carbon

Chalcogenide Glasses

- **Chalcogenide Glasses**
  - Typical Compositions:

Chalcogenide elements,
S, Se, Te to replace oxygen
B_2S_3, SiS_2, P_2S_5 etc
As_2Se_3, As_2Te_3
GeS_2, $GeSe_2$, $GeTe_2$ etc.

- Many different combinations
- Nearly unlimited glass forming systems
- Phase separation is common in many systems
- Typically from synthetic, relatively expensive compounds
- Often sensitive to impurities, oxygen and water

Chalcogenide Glasses

Chalcogenide Glasses

Properties:

- ➢ Low softening points, RT to 300 °C
- ➢ Low chemical durability
- ➢ Potentially toxic
- ➢ Poor optical transmission, typically black
- ➢ Excellent IR transmission

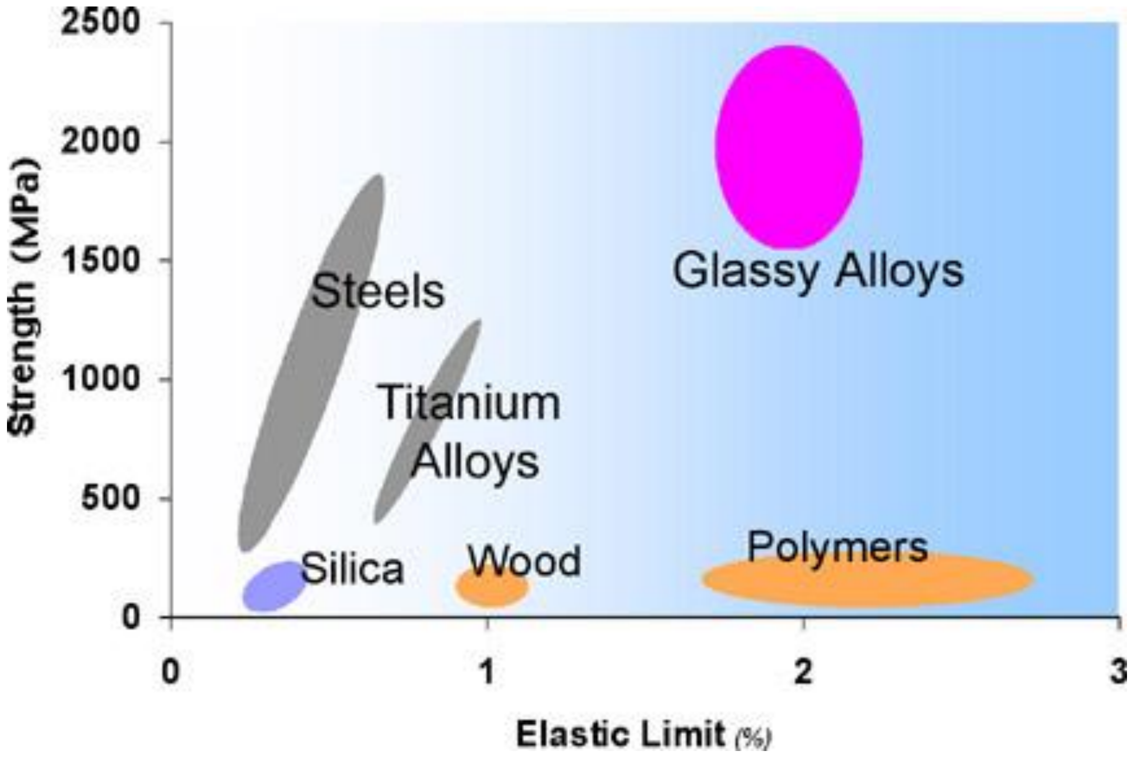
(Heavier atoms and weaker bonding create longer wavelength and hence lower energy transmission)

❑ Photoinduced Phenomena

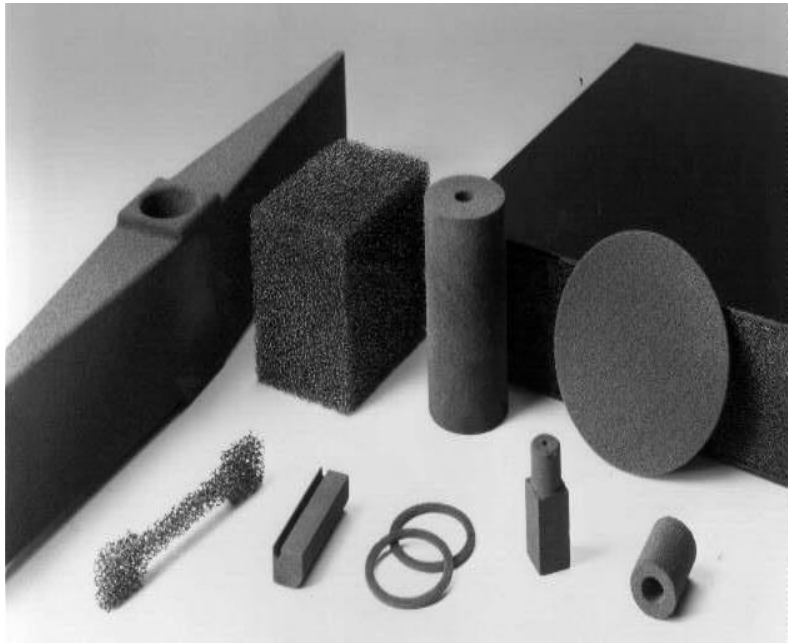
Metallic Glasses

- Metallic glasses lack "compound nature" like oxide and chalcogenide glasses
- Metallic glasses are often multi-component systems near eutectic compositions that are glass forming by rapid quenching
- Zr-Ti-Cu-Ni-Be , Zr-Cu-Ni-Al and Pd-Cu-Ni-P systems,
- $Zr_{41.2}\ Ti_{13.8}\ Cu_{12.5}\ Ni_{10}\ Be_{22.5}$

Metallic Glasses



Vitreous Carbon (Glassy Carbon)



Glassy carbons are disordered phases of carbons with graphite-like bonds interspersed with regions of amorphous carbon.

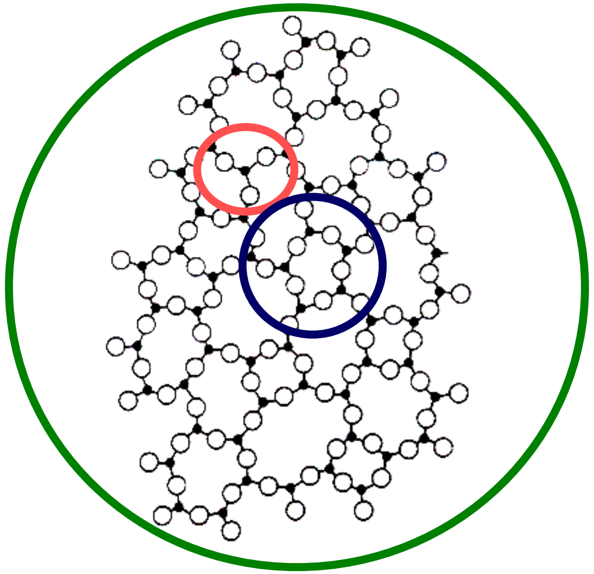
- sp^2 amorphous structure
- Good electrically conductivity
- Good Chemical resistance
- Poor oxidation resistance
- **Mechanical properties:**

  Flexural strength : 260 MPa
  Young's modulus : 35 GPa
  Compressive strength: 580 MPa

The Structure of Glass

- The structure of glass is as varied as the compositions that can be made into glass
- Further complicating the determination of glass structure is that the structure is that of a non-equilibrium material and as such, the structure depends strongly on processing, most often the cooling rate

Different Ranges of Glass Structure

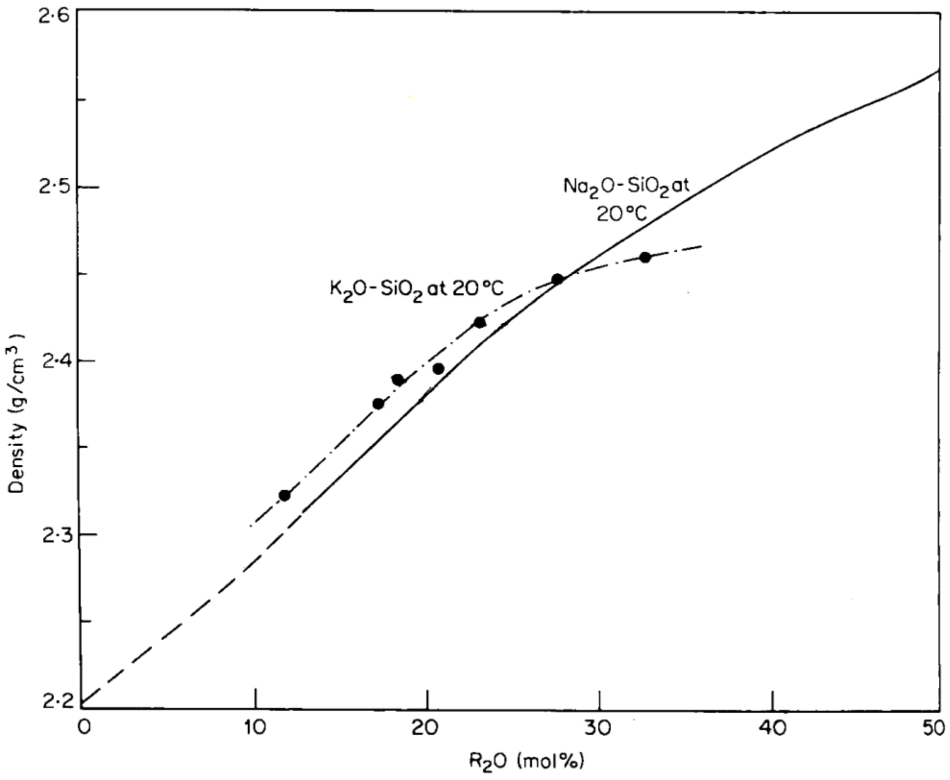


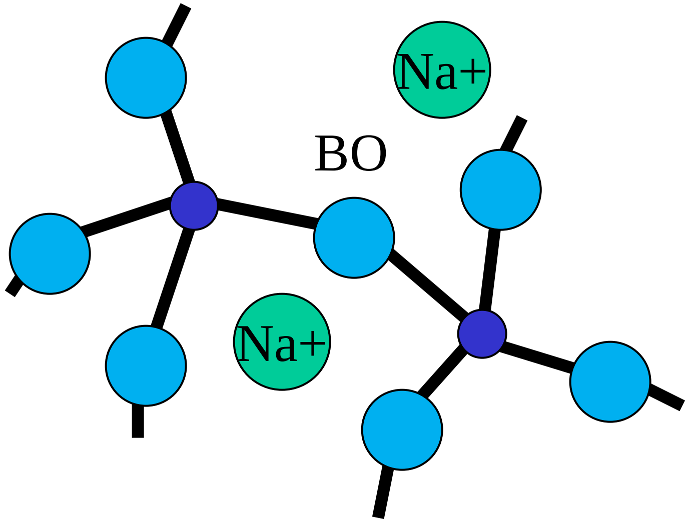
- Short Range Structure
  - 1st coordination sphere
  - Coordination number, bond length, bond angle,
- Intermediate Range Structure
  - 2nd and 3rd coordination spheres
  - Angles between SRO structures
  - Organization of SRO structures into "molecular" structures, e.g... rings and rings sizes
- Long Range Structure
  - Beyond 4 to 5 bond lengths
  - Rarely observed in glass,

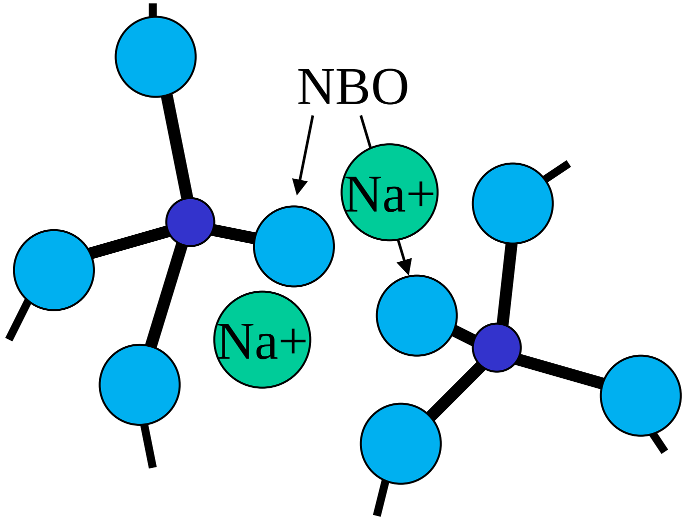
Density of Glass

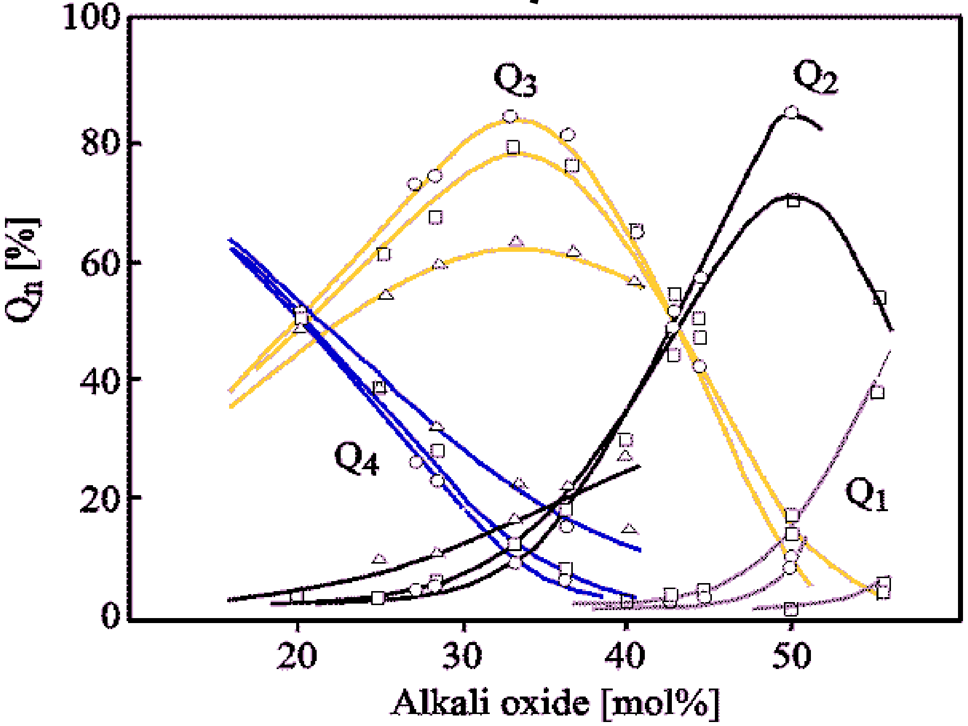
Density of Alkali Silicate Glasses – Effect of Structure

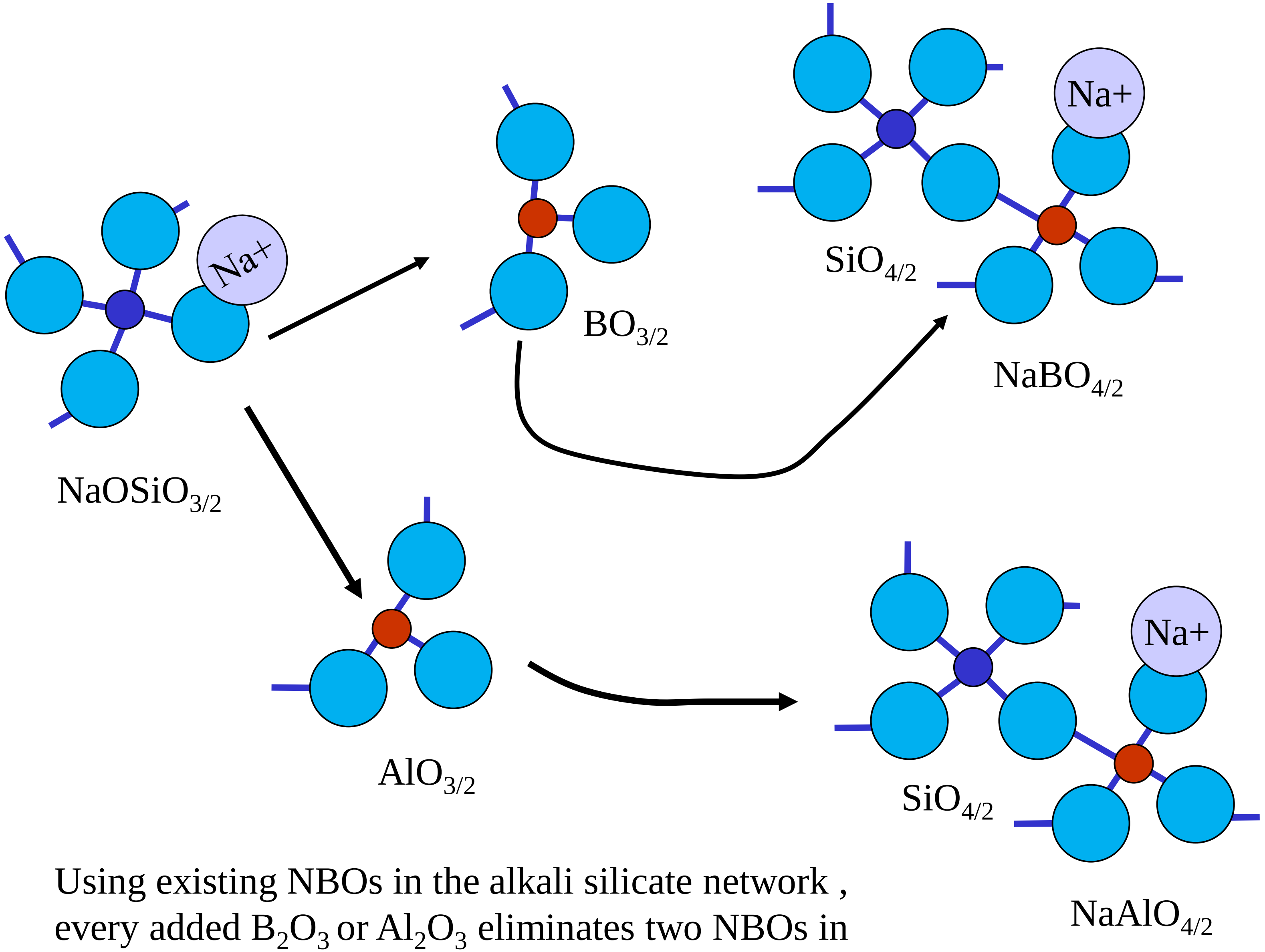
- Density increases with modifier content
- Dependence is linear for low alkali
- Non-linear for higher alkali contents
- Creating non-bridging oxygens at low alkali fractions on Q_3 units
- Structure is a mixture of Q_3 and Q_4 units




BO
Na+
Na+

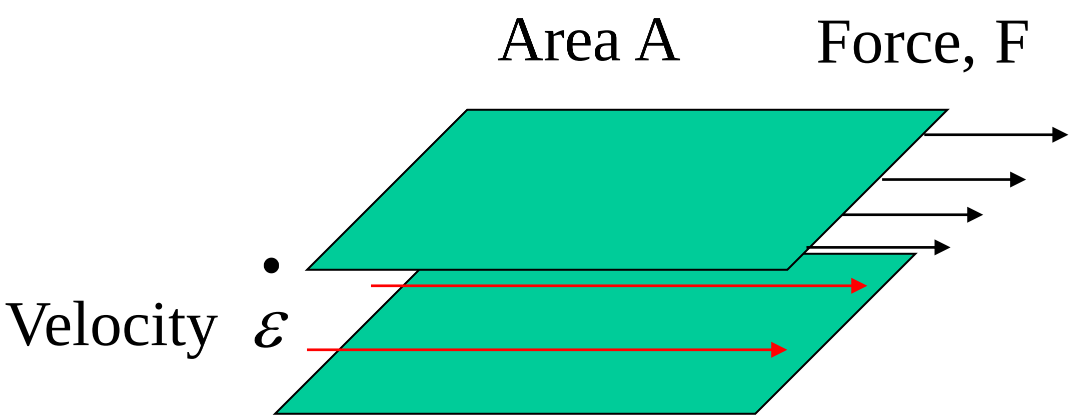

NBO
Na+
Na+


Q3
Q2
Q4
Q1
Q_n [%]
Alkali oxide [mol%]
100
80
60
40
20
0
20
30
40
50



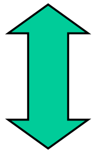
Using existing NBOs in the alkali silicate network , every added B_2O_3 or Al_2O_3 eliminates two NBOs in alkali silicate glasses

Viscosity of Glass



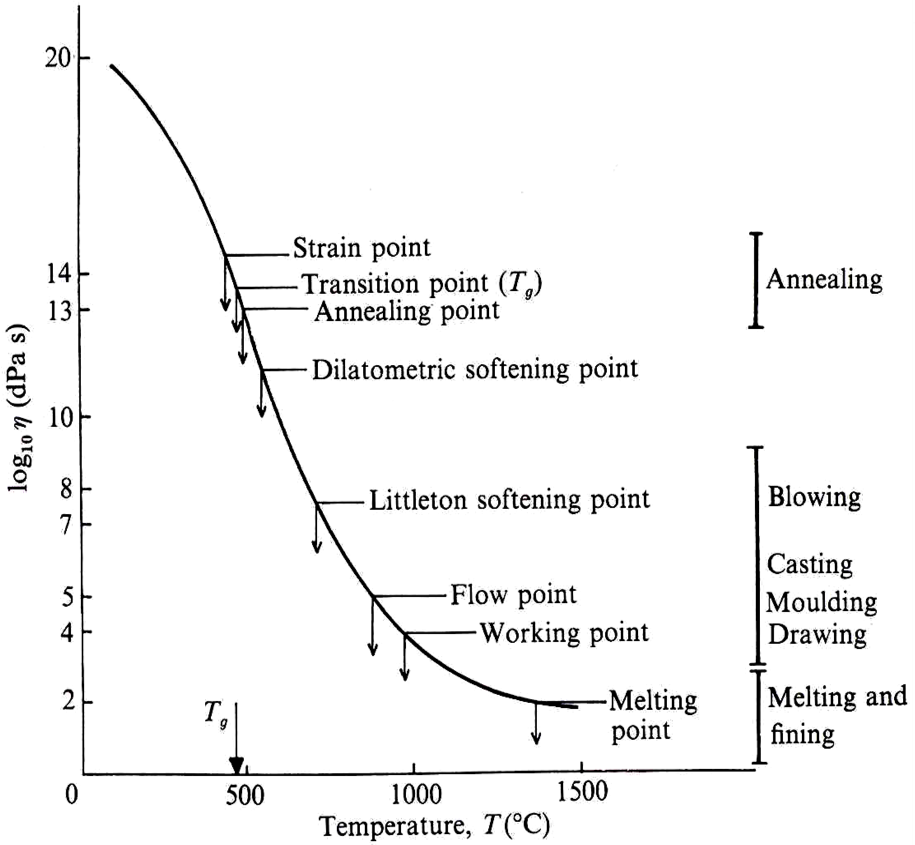
Shear stress required to produce fixed strain rate

The higher the viscosity



The higher the required stress

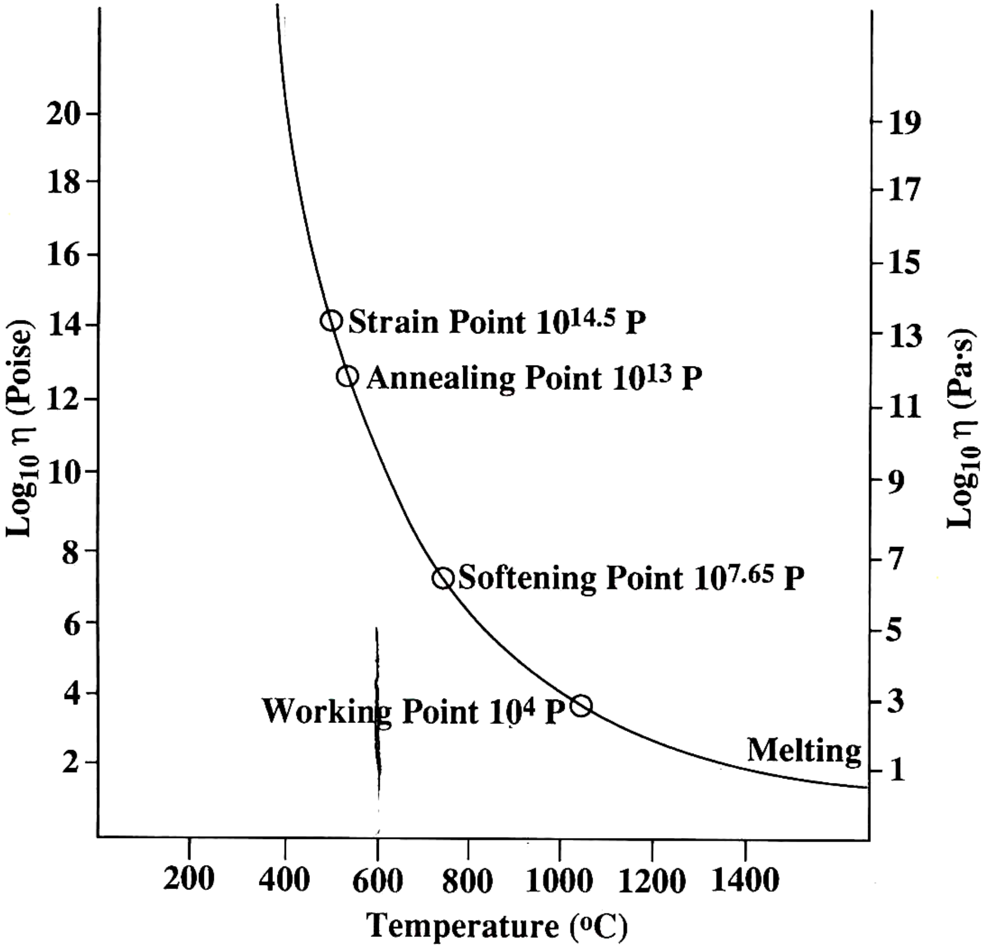
Viscosity at various stages

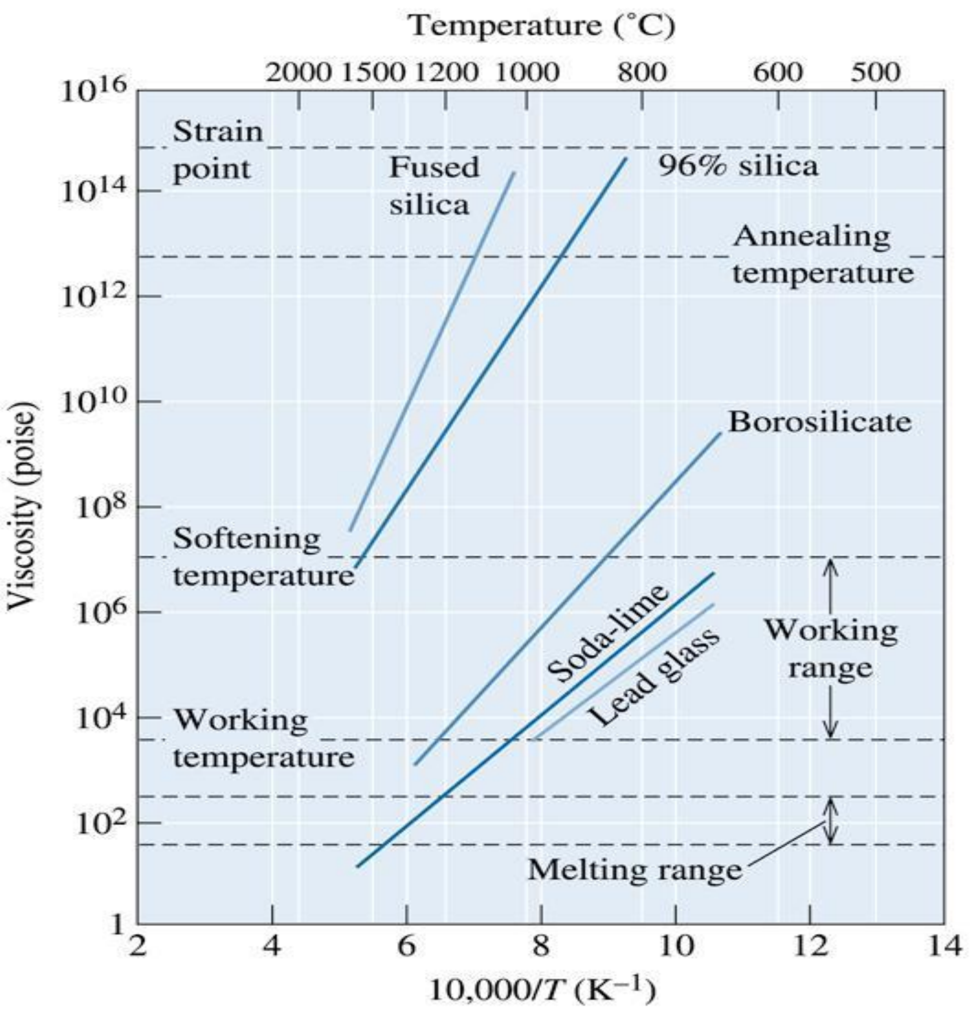


Designation	η (dPa s)
melting point	10^2
working point	10^4
sink point	$10^{4.22}$
flow point	10^5
softening point (Littleton's point)	$10^{7.8}$ (or 4.2×10^7)
dilatometric point	$\sim 10^{11.3}$
annealing point	$\sim 10^{13}$
transition point	10^{13}–$10^{13.6}$
strain point	$10^{14.5}$ (or 3.2×10^{14})

Temperature dependence of viscosity

- Soda lime glass as a common example
- Viscosity decreases rapidly above the annealing point, Tg
- Decreases less rapidly at higher temperatures

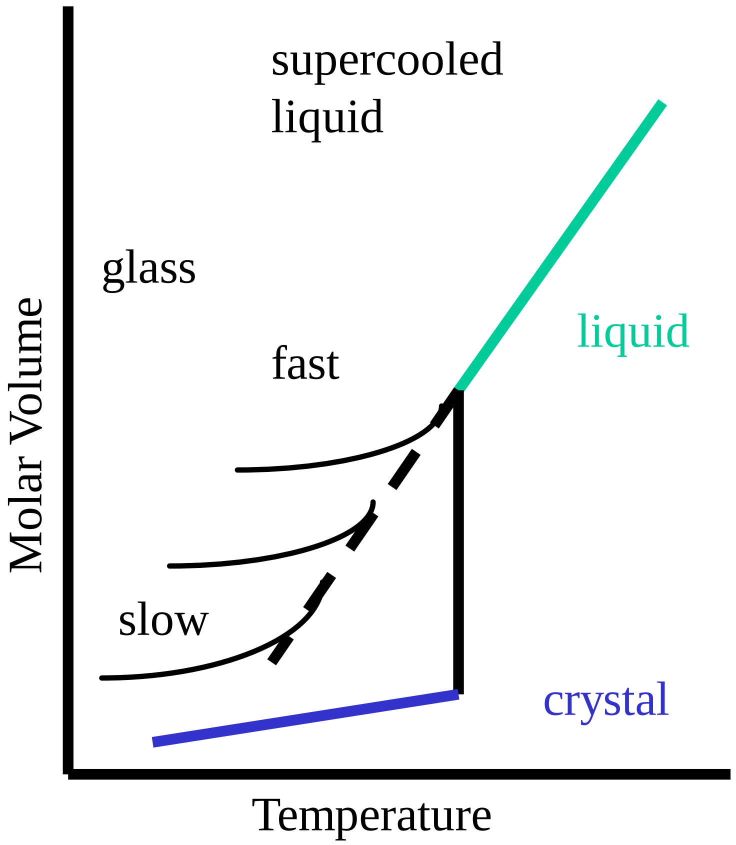




The effect of temperature and composition on the viscosity of glass.

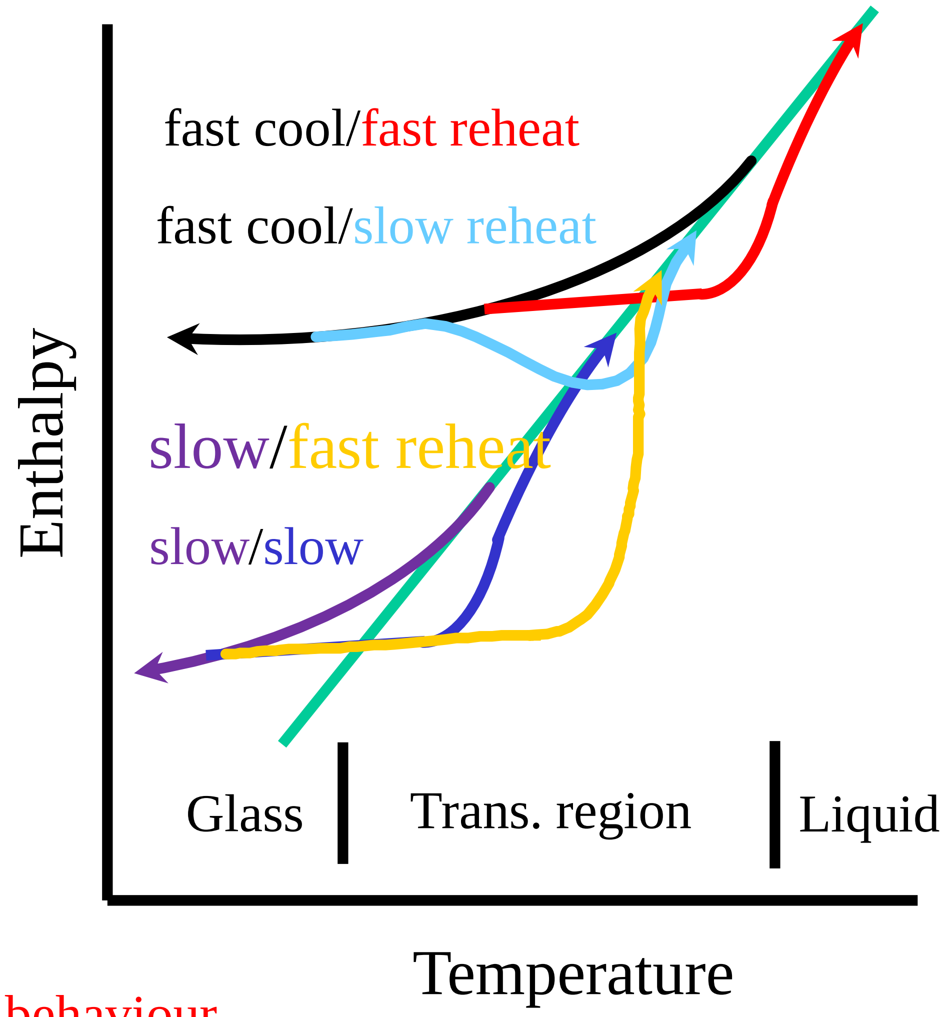
Properties of Glass : Glass Transition Temperature

- The glass transition is the region of temperatures where the properties of a cooled liquid continuously change from being “liquid-like” to “solid-like”
- Structure is continuous with the liquid state
- Properties are continuous with the liquid state
- Glass Transition occurs over a relatively narrow range of temperatures and can be a “sharp” transition in some cases
- Glass forming liquids have a strongly temperature dependent viscosity



The Glass Transition

- The kinetic nature of the glass transition temperature can also be observed when the heating and cooling rates are not equal
  - Experimentally, it is easier to cool at a variable rate and reheat at a constant and instrument calibrated rate, typical 10^{o}C/min
- Fast cooling produces a glass with a higher fictive temperature state
- Slow cooling produces a glass with a lower fictive temperature state
- Maximum difference between heat and cool rates shows this behavior



Well anealed glass does not show this behaviour

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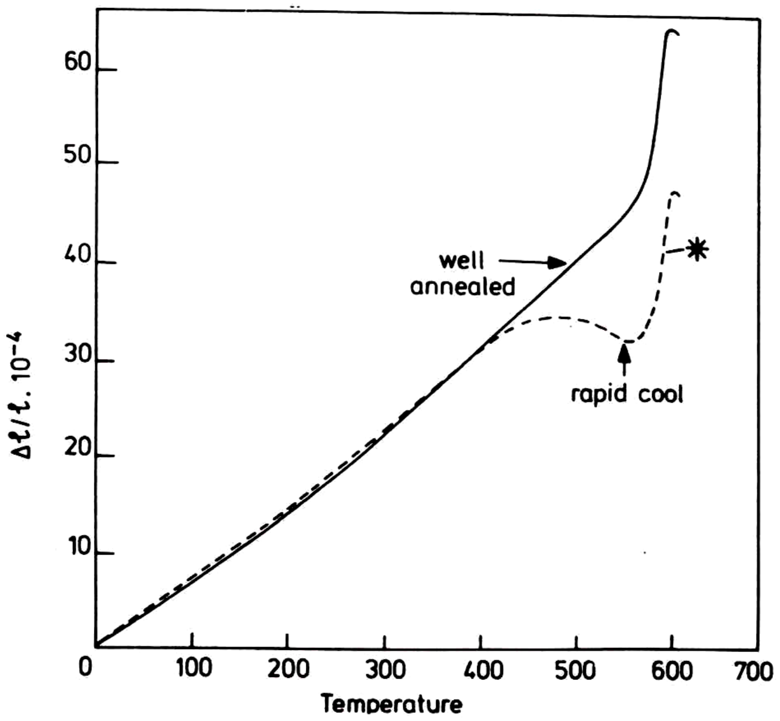
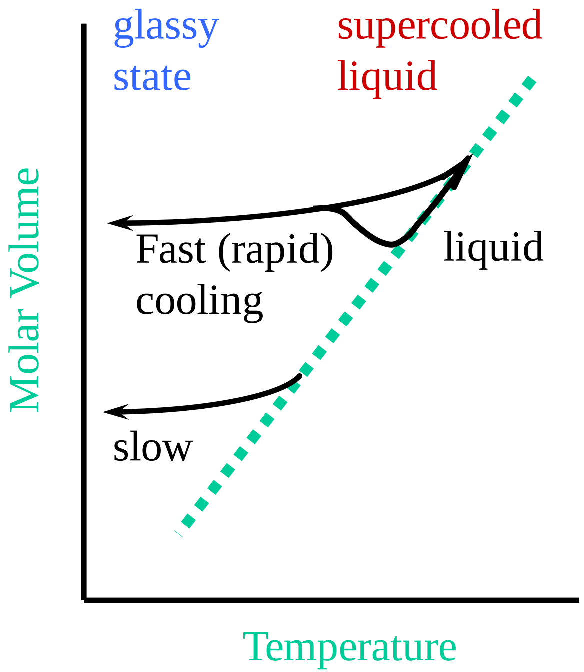
Thermal Expansion of Glass

- Glasses are isotropic
- NBOs increase thermal expansion,
- BOs decrease thermal expansion





As fast cooled glass is reheated and approaches Tg

-The structure begins to “loosen”

-Time is available to relax “down” to the dense structure (slow cooled curve)

Well anealed glass does not show “DIP” behaviour

Thermal Expansion of Glass (Thermal shcok resistance)

- Thermal expansion determines if a glass will be shock resistant, able to withstand high thermal stresses
- Small thermal expansion coefficient leads to high thermal shock resistance
- Large thermal expansion leads to low thermal shock resistance

Glasses are more prone to thermal shock damage when quenched from hot to cold
(Shrinking surface puts center in compresion, surface into tension)
than rapid heating from cold to hot (expanding surface constrained by the center)

Thermal Expansion of Glass (Thermal shcok resistance)

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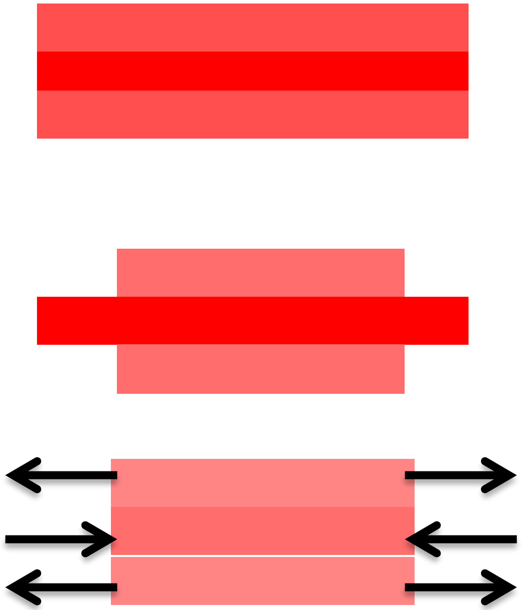
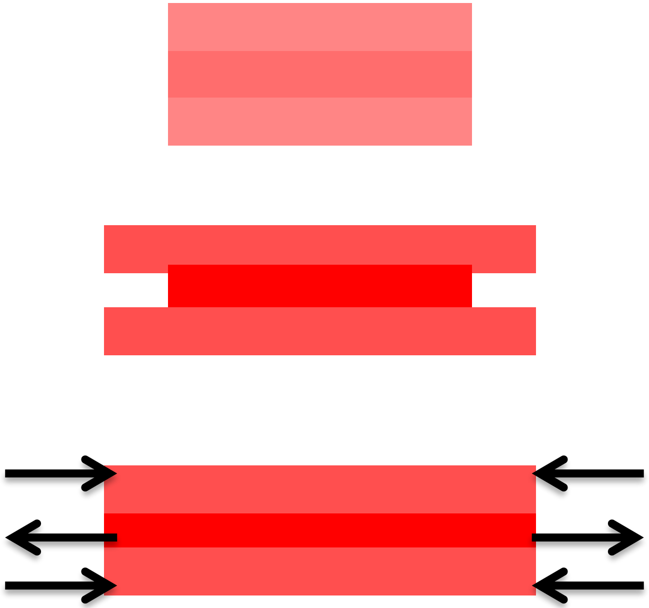
than rapid heating from cold to hot (expanding surface constrained by the center)



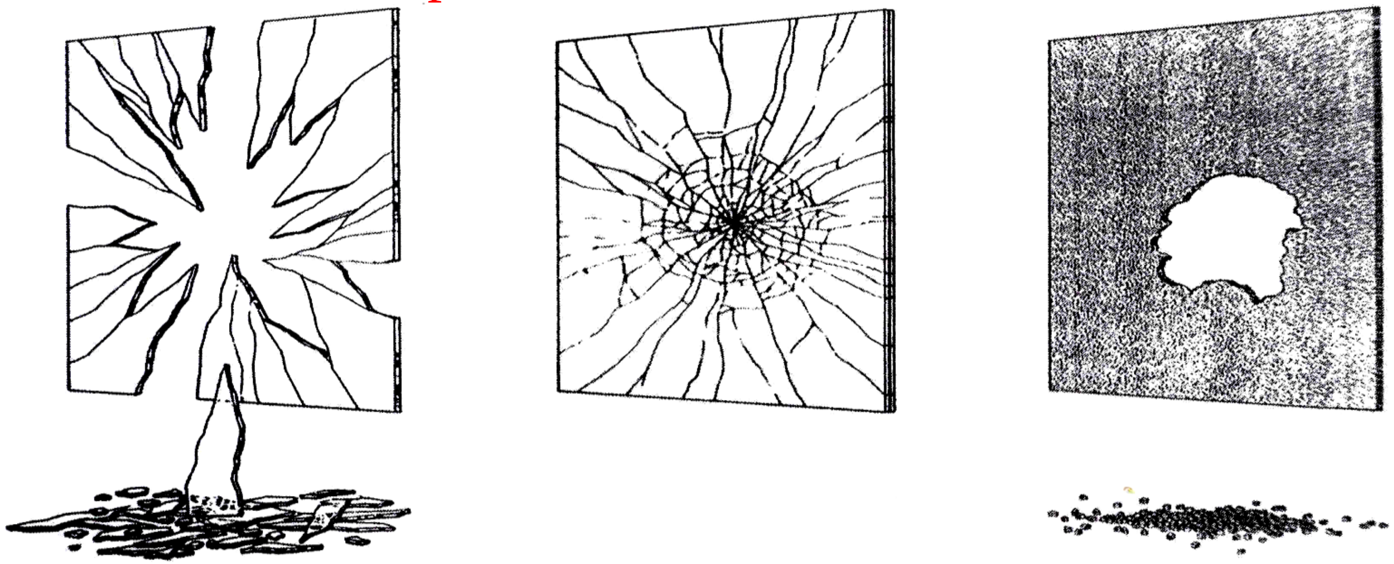
Quench, Hot-to-Cold



Rapid Heat ,Cold-to-Hot

Thermal Expansion of Glass : Tempering Ability

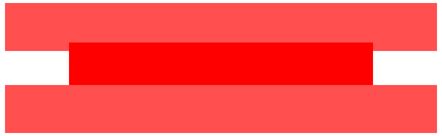
- Thermal tempering increases strength and reduces large dangerous shards to fine small particles



- Thermal Expansion also determines whether a glass can be thermally “tempered” to increase its strength
- High thermal expansion leads to high tempering ability
- Low thermal expansion leads to low tempering ability

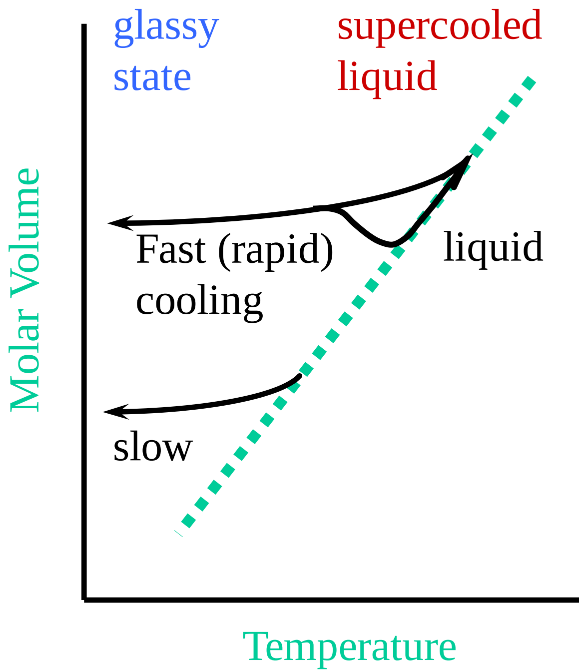
Thermal Expansion of Glass : Tempering Ability

Uniform Heat, T > Tg



Quench to RT,
Center would shrink to smaller dimension (lower T-fic)

Constrained by surfaces
Center goes into tension
&
surface into compression

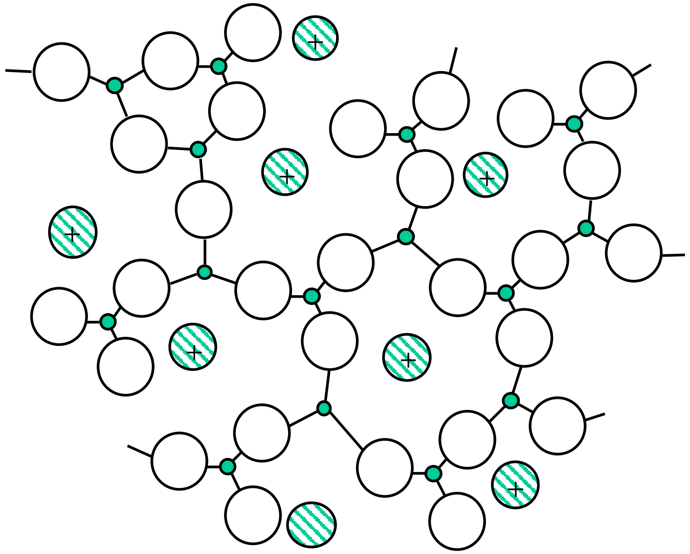


Properties of Glass :Chemical Durability

- All common applications of glass require good chemical durability
- Soda lime glasses for the most part are very chemically durable
  - Most acids, bases, all organics
  - Exceptions include hydrofluoric acid
- Chemical durability results from strong covalent bonding
  - Numerous -O-Si-O- BOs and
  - Relatively few –Si-O^- Na^+ and –Si-O^- $^+Ca^+$ $^-$O-Si-O- NBOs
  - Strong thermodynamically stable SiO_2 accounts for the chemical stability of most silicate glasses

Mechanisms of Chemical Attack of Glass

- **Leaching** of “mobile ions” out of the glass
  - $\equiv$Si-O$^-$ Na$^+$, weakly bound alkali ions leach from glass in water
  - $\equiv$Si-O$^-$ Na$^+$ + H$^+$..OH$^-$ >> $\equiv$Si-O$^-$H$^+$ + Na$^+$ OH$^-$(aqueous)



Typical Rankings of Durability of Glasses

- Glasses with least NBOs, most BOs are the most durable
- Glasses which have NBOs eliminated through the addition of Al_2O_3 or B_2O_3 have better durabilitites at constant silica fraction
- Glasses with most alkali are the least durable
- Glasses with the heavier, larger alkali, K, Rb, Cs etc are the least durable of all

Properties of Glass :Dielectric Properties

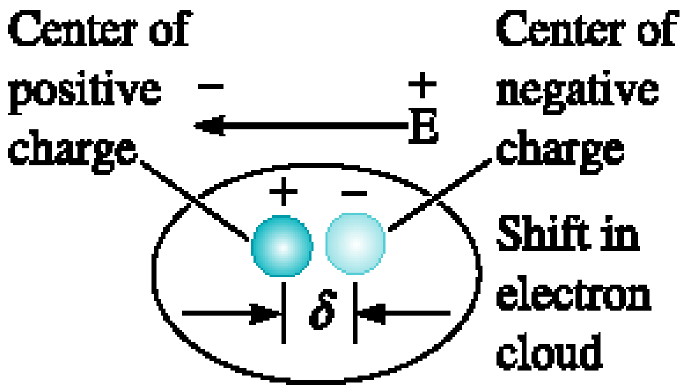
Dielectric response of glass

- Dielectric response is the movement of bound charges over relatively short distances
- Polarization is where bound charges move short distances but do not *conduct*
- Dipole moments are examples of "built-in" polarization in glass
  - $\equiv Si(\delta^{+})\text{-}O(\delta^{-})\text{-}$
  - Silicon oxygen bond is a dipole moment, charge separated a distance
- Applied electrical fields to a glass can *polarize* atoms, ions, bonds and molecular structures in glass to cause a dielectric response by the glass
- Glass can have different types of polarization or dielectric responses

Different Mechanisms of Polarization in a Glass

- Electronic polarization occurs at the atomic level

  - Electron cloud around the atom polarizes in response to applied electric field
  - Larger atoms, more electrons farther from the nucleus, polarize more
  - Smaller atoms, fewer electrons closer to the nucleus, polarize less
  - Tellurium has a higher atomic polarizability than Oxygen
  - $O^{=}$ has a higher polarizability than Si^{+4}



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Atomic Polarizability in Glass

- Polarizability increases as AW increases

Table 27.1

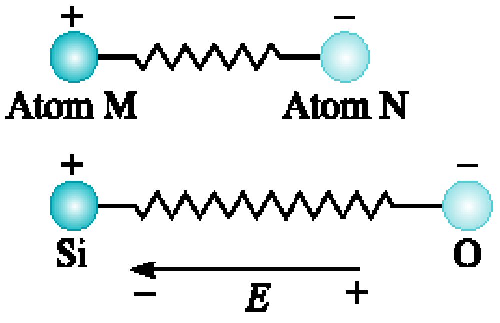
ATOMIC POLARIZABILITIES OF THE HALOGEN IONS, NOBLE GAS ATOMS, AND ALKALI METAL IONS[a]

HALOGENS		NOBLE GASES		ALKALI METALS	
		He	0.2	Li^+	0.03
F^-	1.2	Ne	0.4	Na^+	0.2
Cl^-	3	Ar	1.6	K^+	0.9
Br^-	4.5	Kr	2.5	Rb^+	1.7
I^-	7	Xe	4.0	Cs^+	2.5

[a] In units of 10^{-24} cm^3. Note that entries in the same row have the same electronic shell structure, but increasing nuclear charge.
Source: A. Dalgarno, *Advances Phys.* 11, 281 (1962).

Bond Polarization in Glass

- Non-Covalent bonds have built in polarizations that can be increased in the presence of an electric field
- Positive and negative ends of the dipole are polarized in opposite directions by the applied field
- Strong bonds that have small dipole moments, little separation of charge over short distances, have small bond polarization
- Weak bonds that have large dipole moments, larger charge separation over larger distances, have larger bond polarization



Bond Polarization in Glass

- C-H is quite covalent, little charge separation, strong bond, little bond polarization
  - Polymers have low dielectric constants
- Na_2O and CaO are more ionic and therefore create greater bond polarizability
  - Ionic compounds have larger dielectric constants

Table 27.3

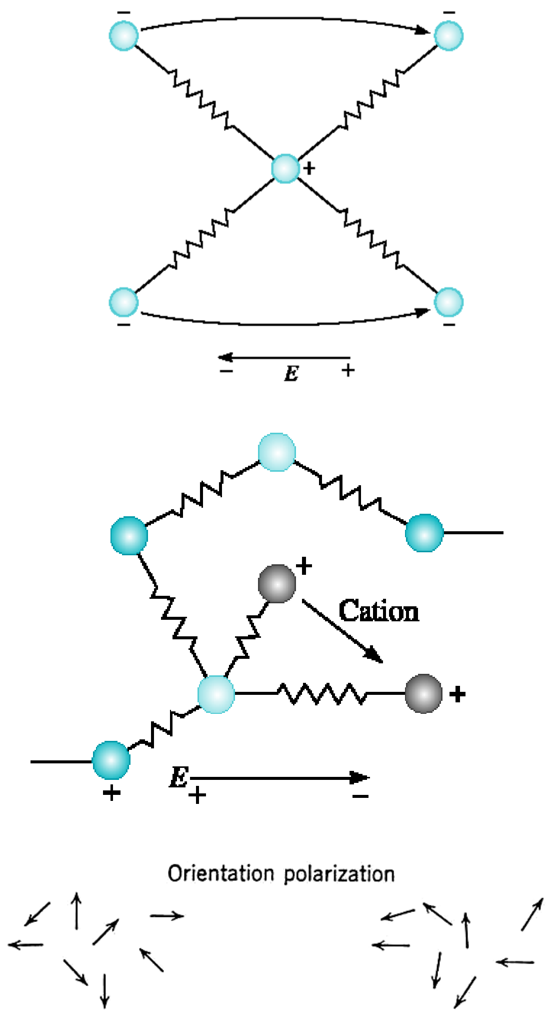
STATIC DIELECTRIC CONSTANTS FOR SELECTED COVALENT AND COVALENT-IONIC CRYSTALS OF THE DIAMOND, ZINCBLENDE, AND WURTZITE STRUCTURES[a]

CRYSTAL	STRUCTURE	ϵ_0	CRYSTAL	STRUCTURE	ϵ_0
C	*d*	5.7	ZnO	*w*	4.6
Si	*d*	12.0	ZnS	*w*	5.1
Ge	*d*	16.0	ZnSe	*z*	5.8
Sn	*d*	23.8	ZnTe	*z*	8.3
SiC	*z*	6.7	CdS	*w*	5.2
GaP	*z*	8.4	CdSe	*w*	7.0
GaAs	*z*	10.9	CdTe	*z*	7.1
GaSb	*z*	14.4	BeO	*w*	3.0
InP	*z*	9.6	MgO	*z*	3.0
InAs	*z*	12.2			
InSb	*z*	15.7			

[a] Quoted by J. C. Phillips, *Phys. Rev. Lett.* **20**, 550 (1968).

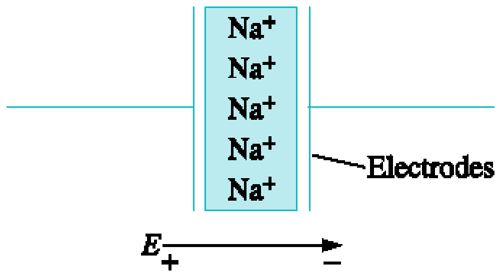
Orientation Polarization in Glass

- Molecules can rotate and rearrange in an electric field
- Orientation polarization can give rise to very large dielectric constants
- Water has a dielectric constant of 80 because it can reorient its dipole in the electric field
- Glasses are rigid below Tg and unless they contain lots of water or other molecules do not exhibit large reorientation polarizations



Space Charge Polarization in Glass

- Glasses do possess mobile cations
- Weakly bound at NBO sites
- Diffusion from one site to another
- Cations move in one favored direction
- Create “Space” full of “Charge”
  - A space charge region
- Glasses with large fractions of mobile cations create largest space charge polarization
- Glasses with no mobile cations cannot create space charge polarization



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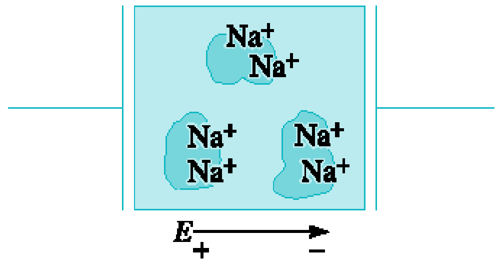
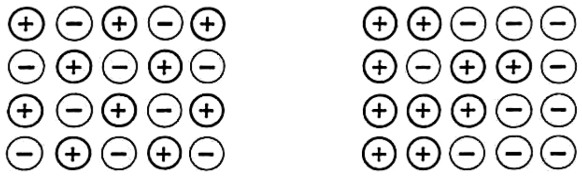
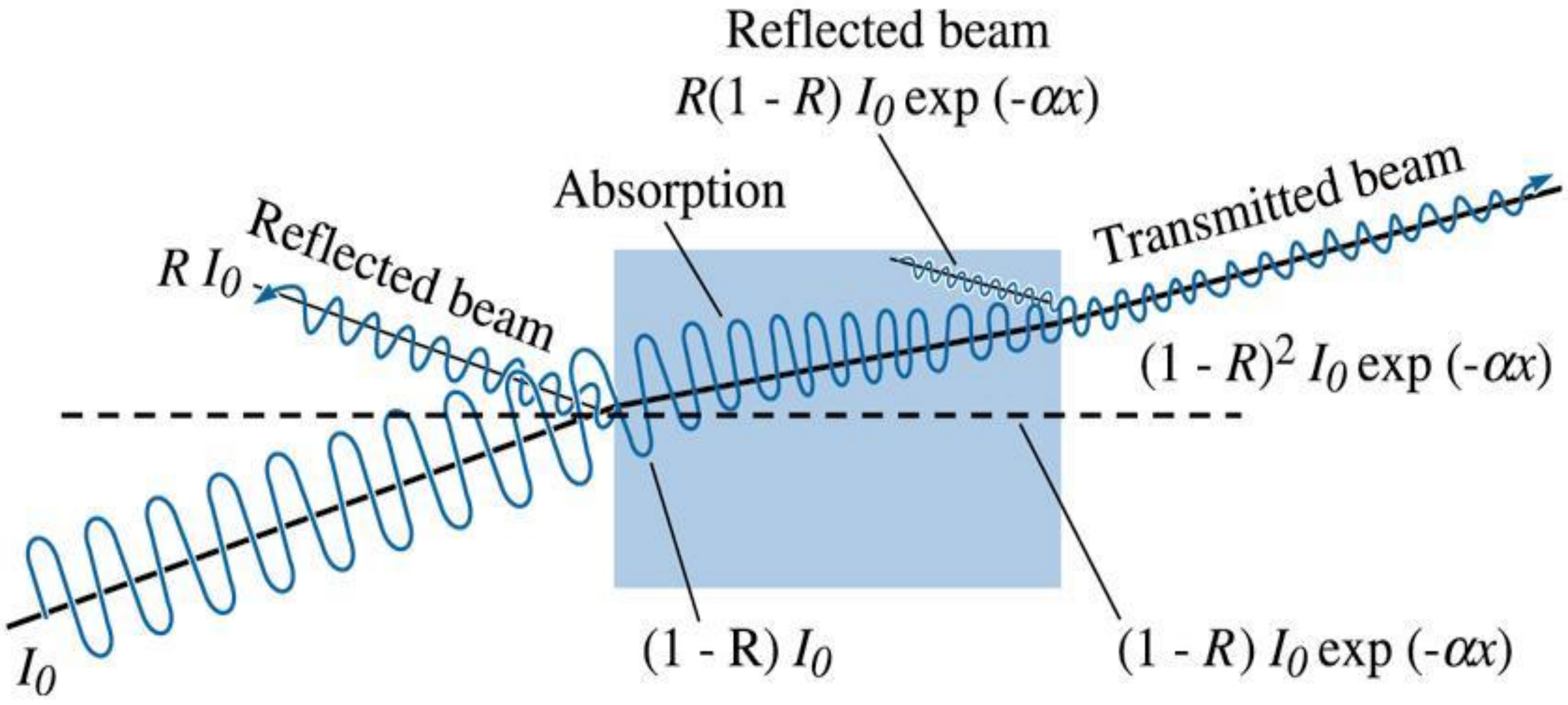


Space charge polarization



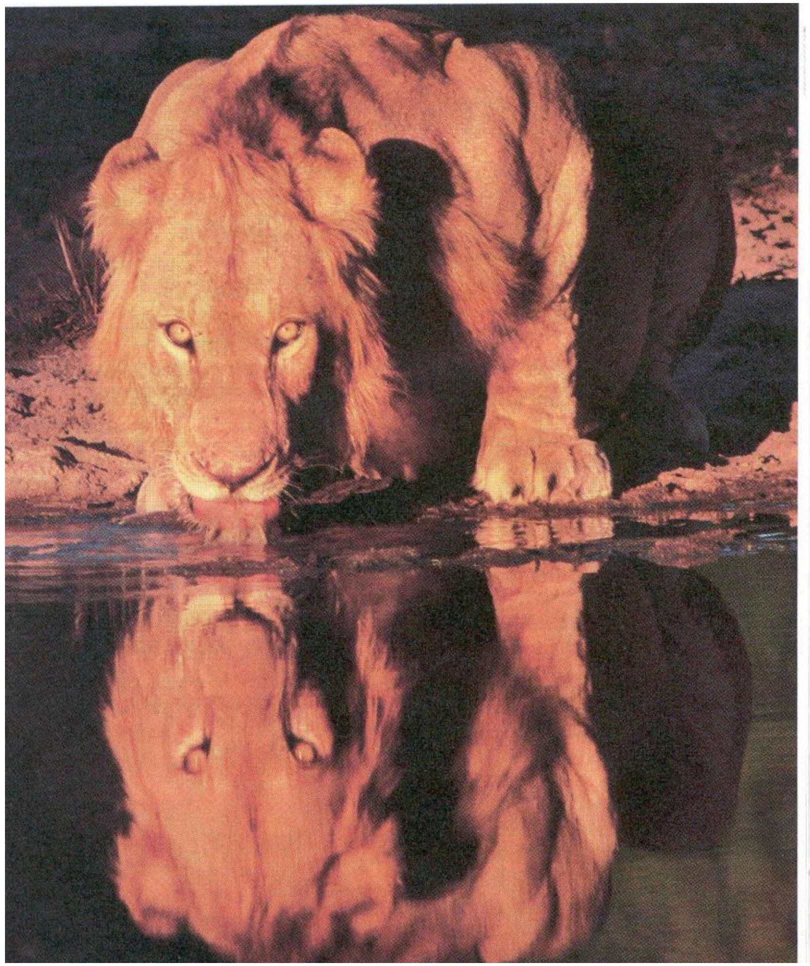
Optical Properties of Glass

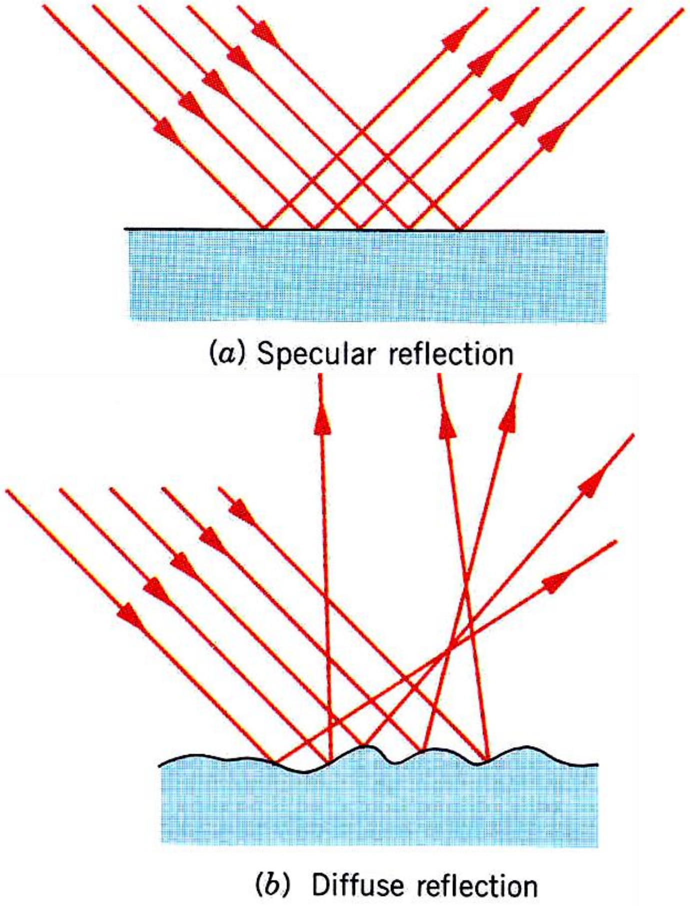


Fractions of the original beam that are reflected, absorbed, and transmitted.

Optical Properties of Glass : Passive Optics

- Reflection, Refraction, and Absorption





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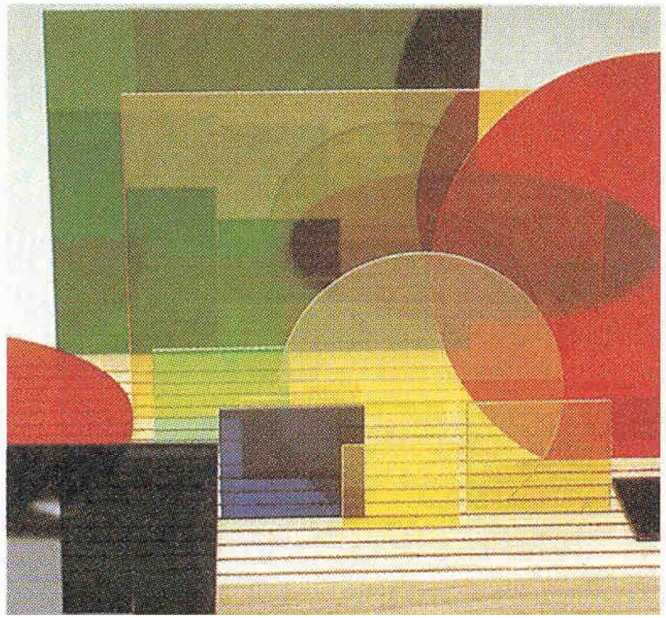
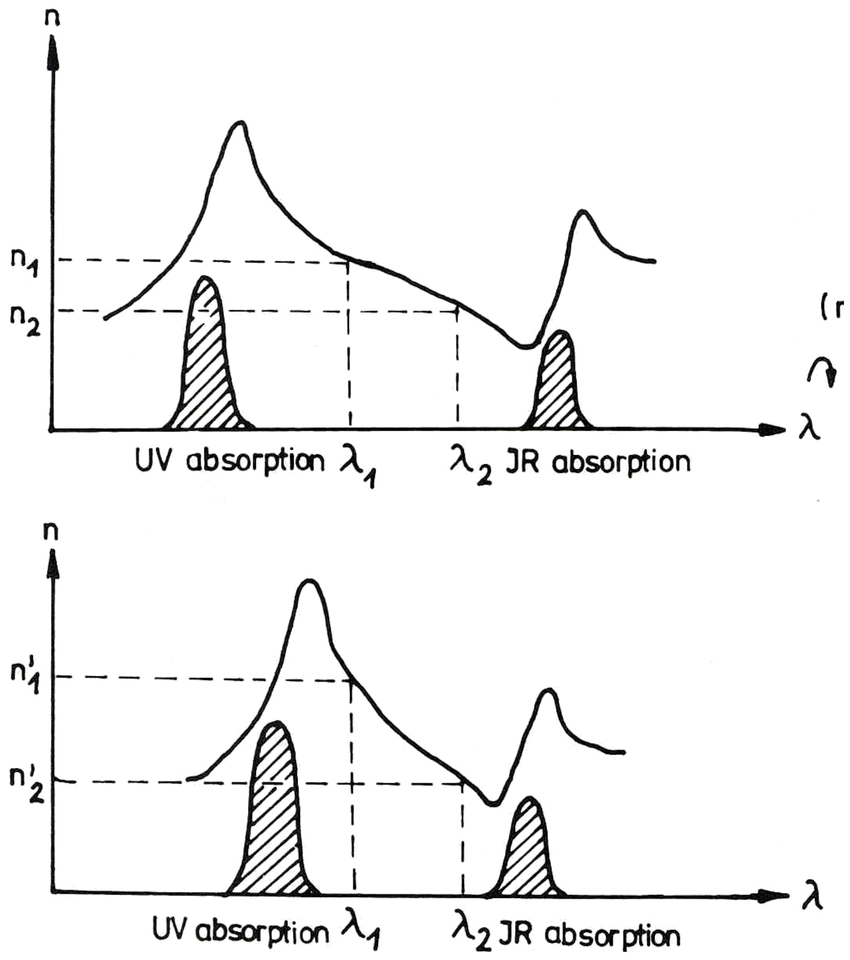
Color in Glass



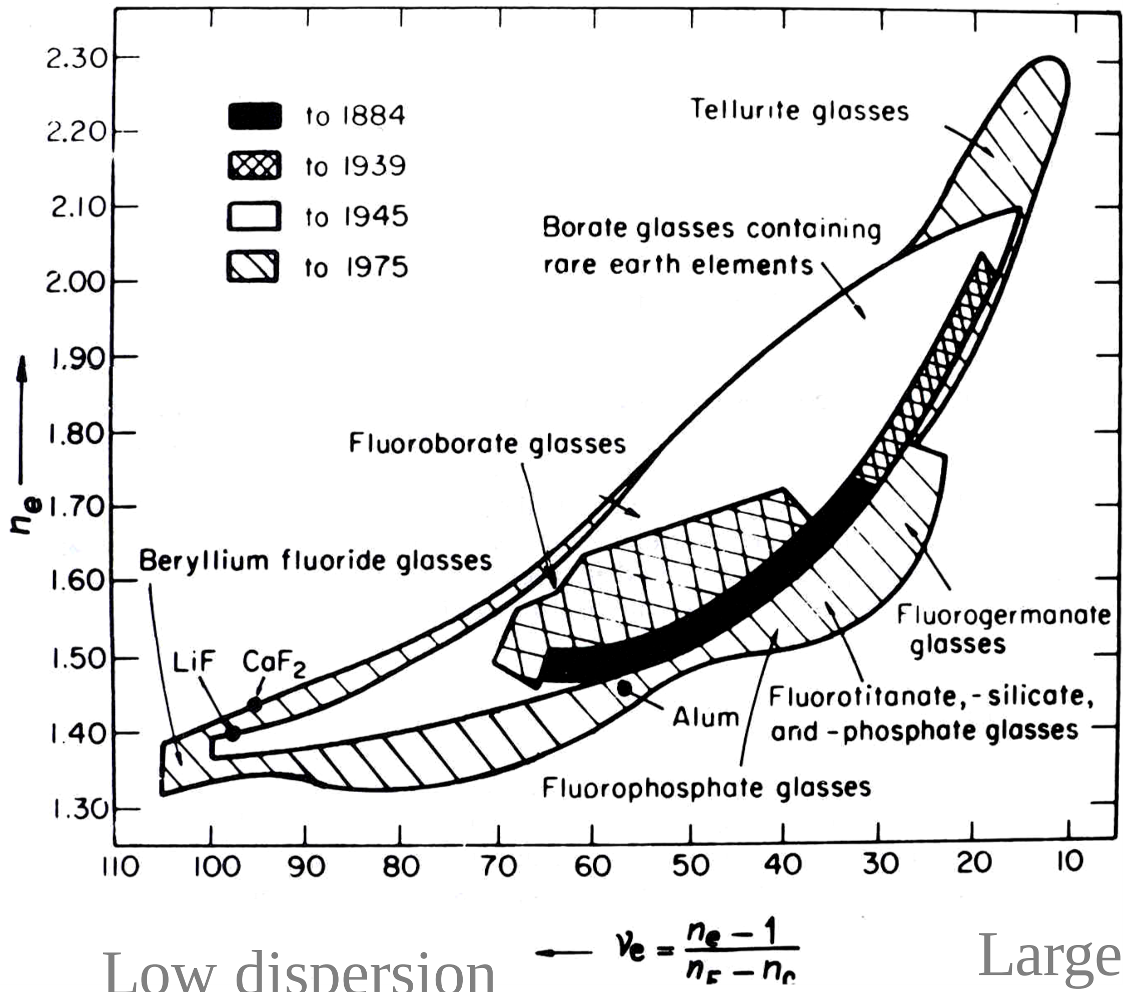
Spectral Dependence of Index of Refraction



- Index of Refraction is wavelength dependent
- Increasing sharply in the region of absorption in the glass
  - Short wavelength is the visible/UV cutoff of the glass
  - Long wavelength is the IR cutoff of the glass
- At these two "resonance"points index of refraction shows absorption or resonance effects
- The wider the transmission window of the glass, the smaller the wavelength dependence.

Abbe number quantifies the λ dep. of n

High n



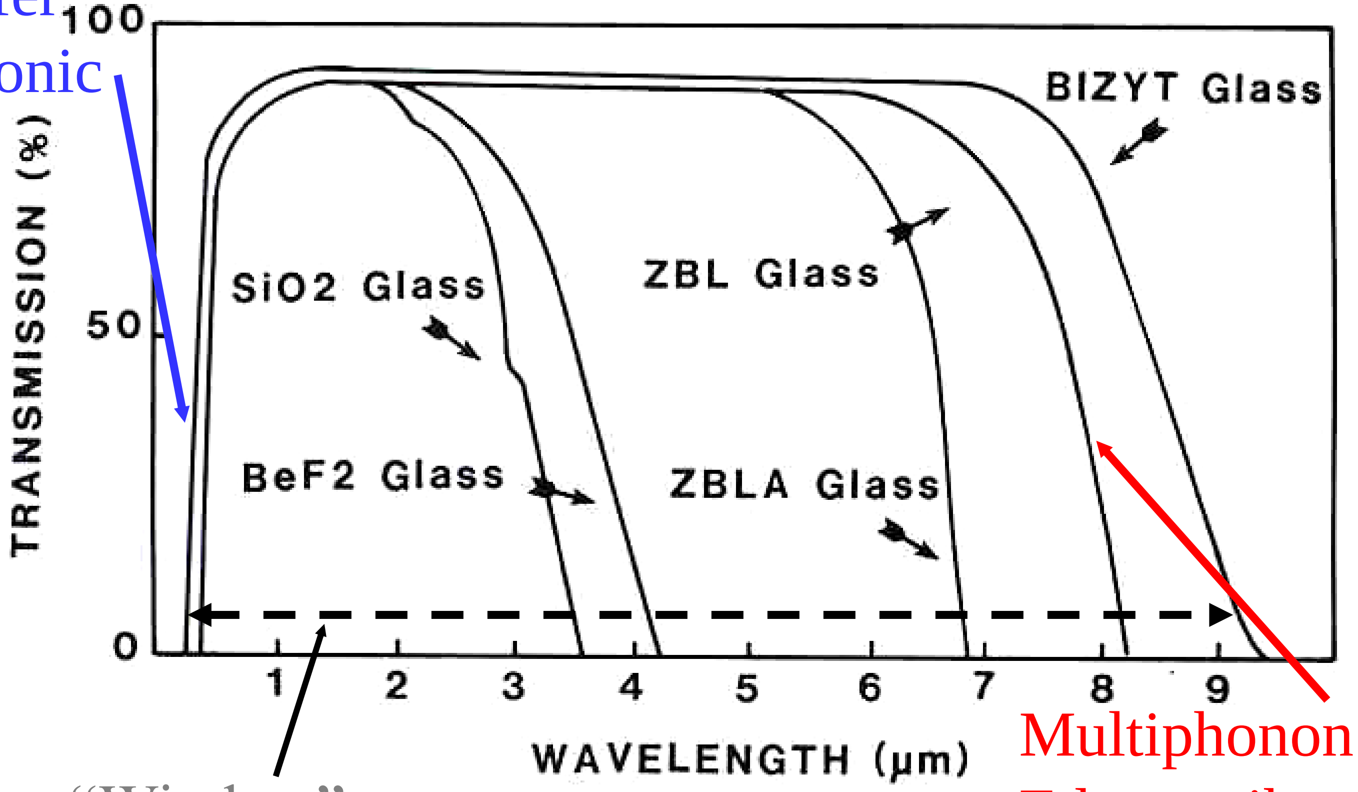
Low n

Low dispersion

Large dispersion

Optical Transmission "Window" of Glass

Charge transfer edge – electronic absorption

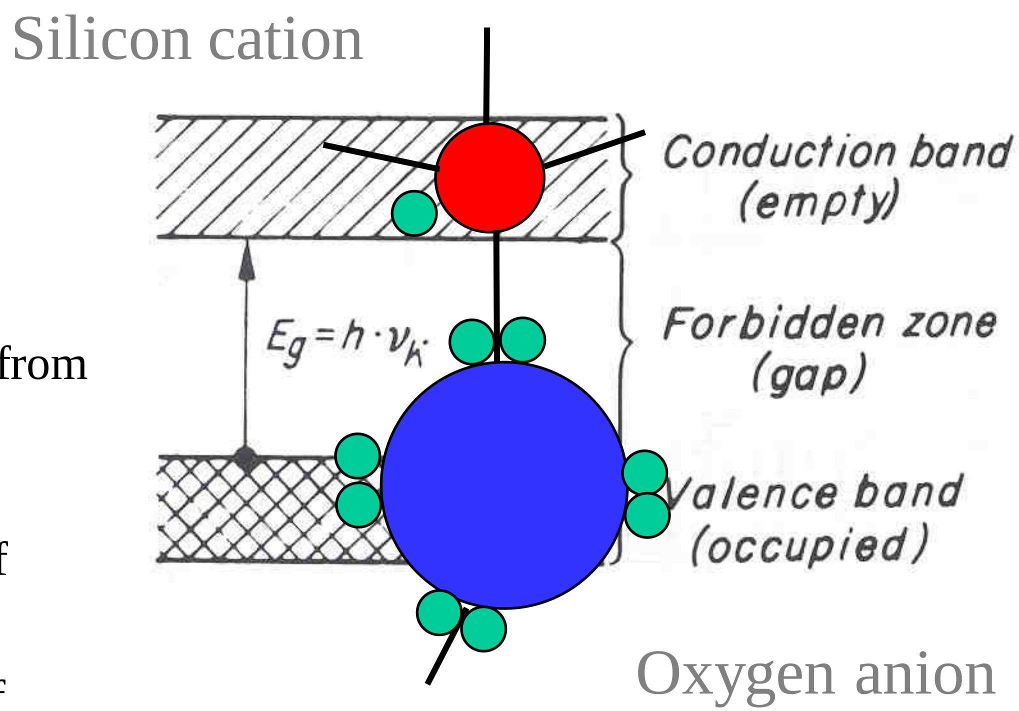


Transmission "Window"

Multiphonon Edge – vibrational absorption

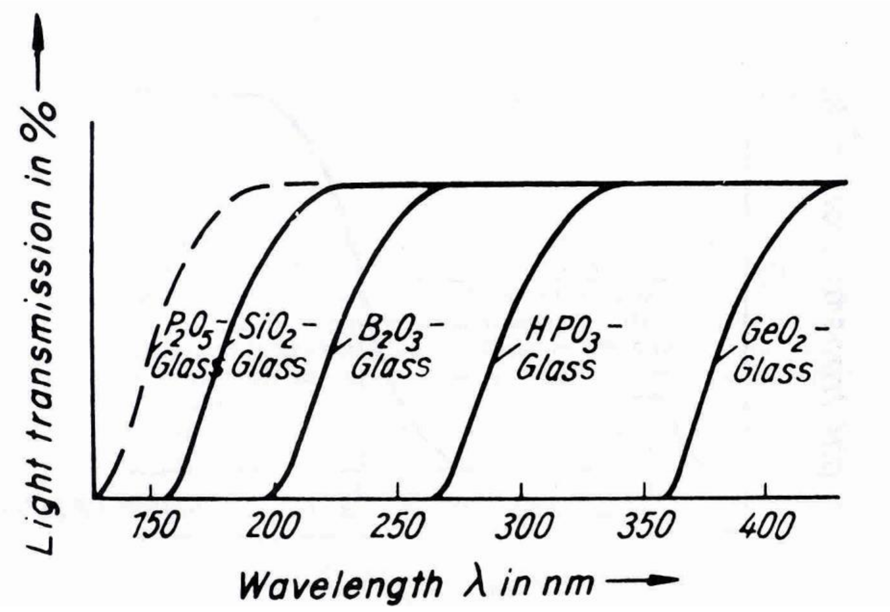
Short Wavelength Edge

- Short wavelength edge
  - UV edge, UV cutoff
  - Urbach edge
  - Charge Transfer band
- Arises from electronic absorption from light hitting the glass
  - Tightly bound electrons
    - Shorter wavelength cutoff
  - Less Tightly bound electrons
    - Longer wavelength cutoff
- Charge transfer band
  - Because electrons promoted from where they are to where they aren't
  - Anions(e- rich) to cations(e^- poor)



UV Edge for various base glass formers

- Transmission edge shifts
  - To shorter wavelengths
  - The stronger the electronic bonding
  - The higher the elements are on the periodic table
- The transmission edge shifts
  - To longer wavelengths
  - The weaker the electronic bonding
  - The lower the elements on the periodic table
- SiO_2 is used heavily in UV “writing” in photolithography
  - 0.10 microns = 100 nm!



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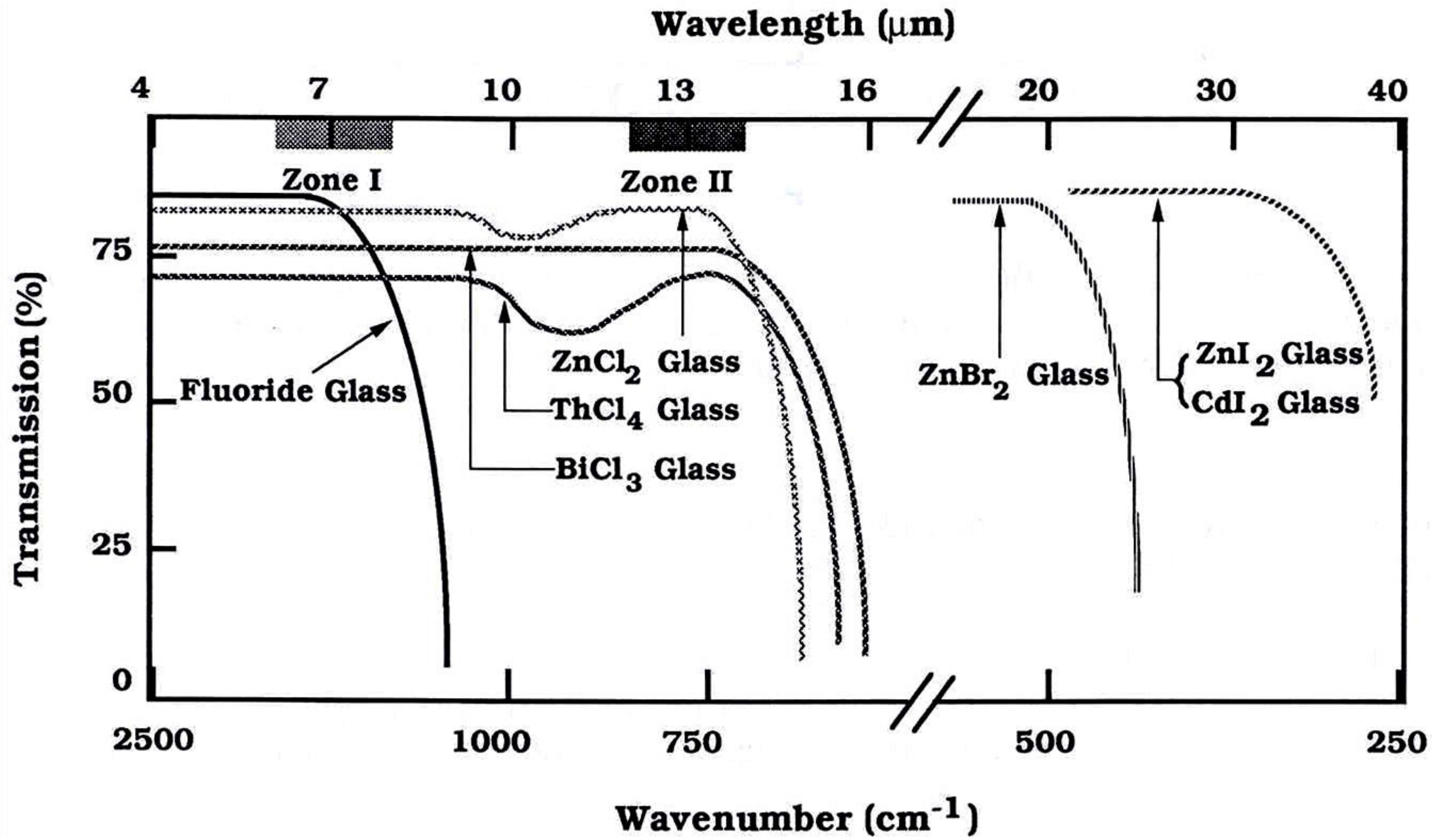
Long wavelength (vibrational) edge of glass

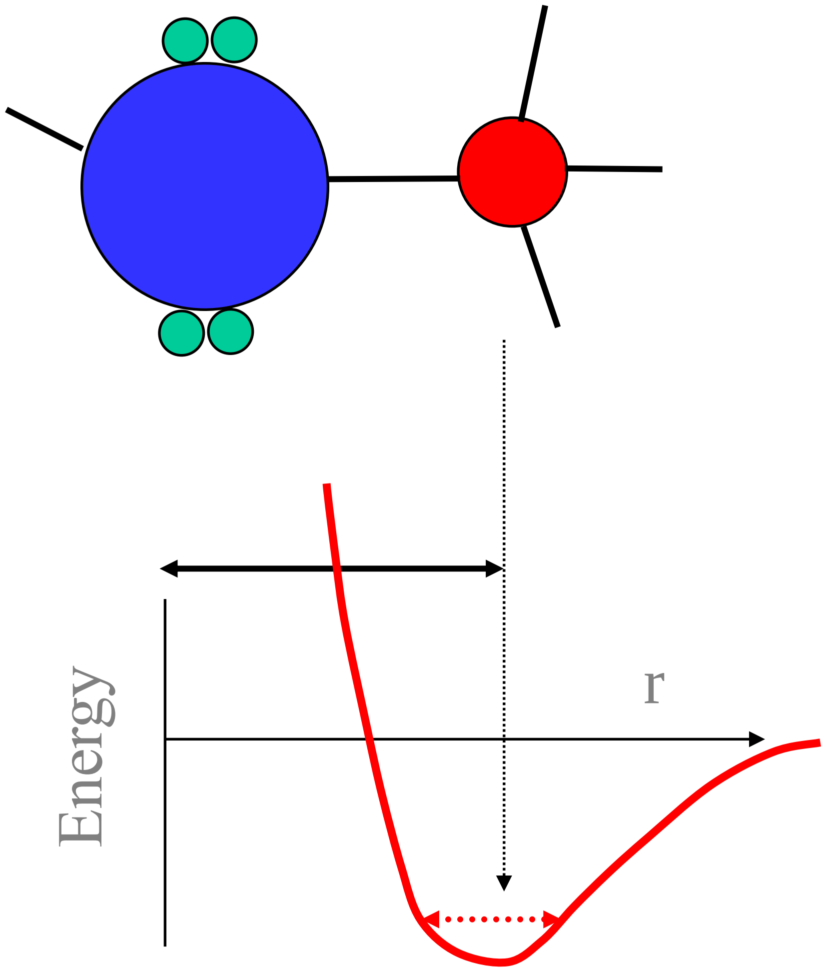


Vibrational Absorption in Glass

- Vibrational Edge
  - Multiphonon edge
  - Arises from vibrational absorption in glass

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

- Vibration frequency increases with
  - Bond force constant (k)
  - Bond strength
  - smaller reduced masses
  - $\mu = (m_1 m_2)/(m_1 + m_2)$

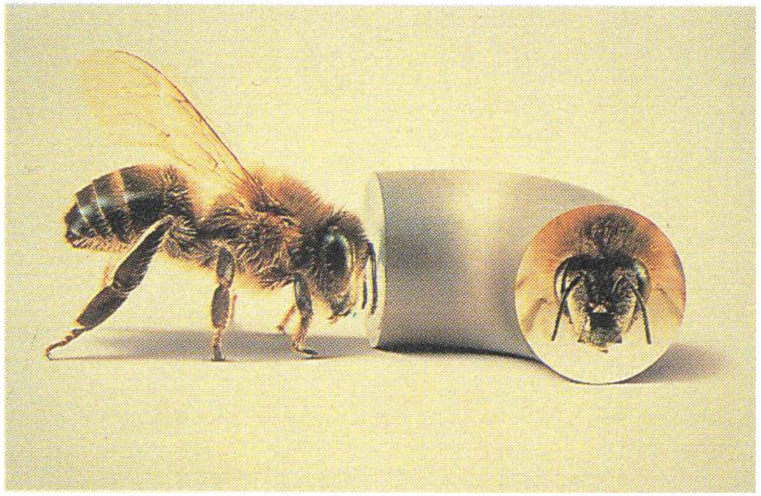


Properties of Glass

Active Optical Properties of Glass

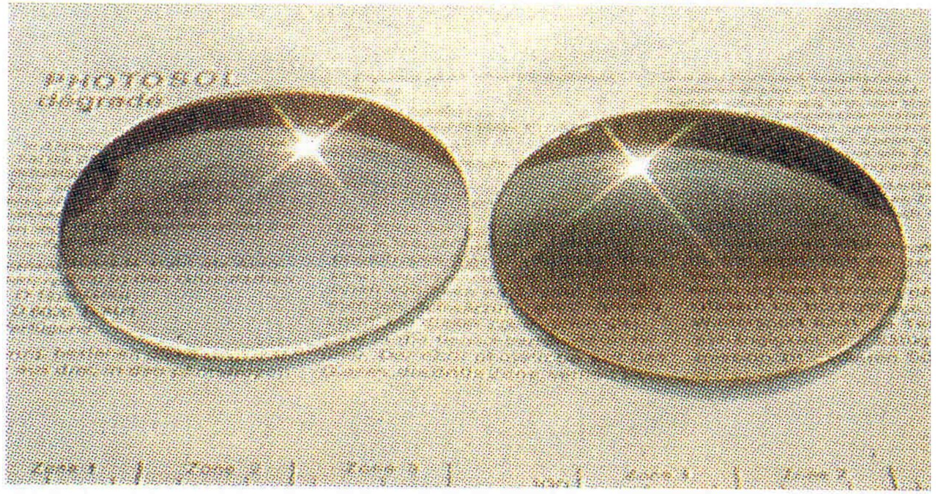
Passive versus Active Optical Properties of Glass

Passive Transmission Optics



Response is time independent

Active Transmission Optics



Response is time dependent

Typical Active Responses of Glass

- Active Absorption
  - Absorption and Transmission response of glass is time dependent
- Active Refraction
  - Refraction and index of refraction response of glass is time dependent
- Active Emission
  - Optical emission of glass is time dependent
  - Fluorescence – fast emission of light
  - Phosphorescence – slow emission of light

➢ Photochromic glasses
  - Darkening sunglasses
  - Optical Amplifiers

➢ Non-Linear index of refraction
  - Optical Switches
  - Fiber-Bragg Gratings

➢ Light Amplification by Spontaneous emission (Laser)
  - Glass-based laser hosts

Properties of Glass :

Mechanical Properties of Glass

Elastic Properties and Strength

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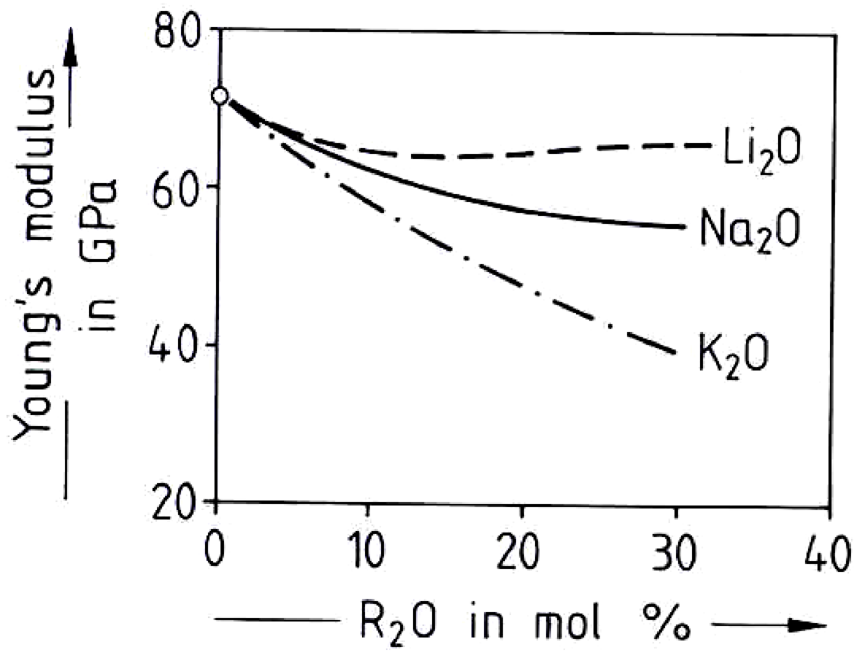
Mechanical Moduli for Alkali Silicate Glasses

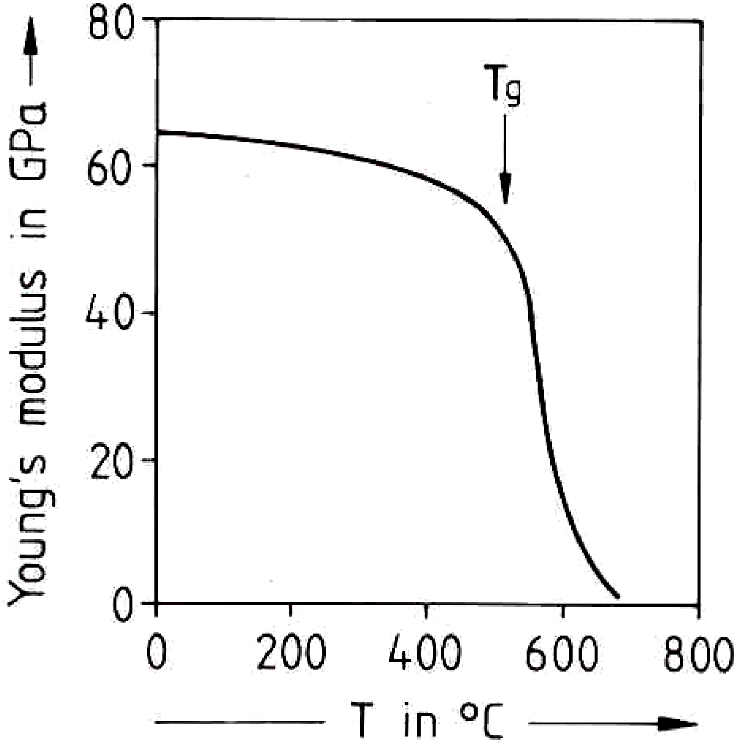
- Modulus decreases as alkali modifier increases
- Modulus decreases with increasing fraction of NBOs
- Modulus decreases with field strength of the cation
- $Li^+ > Na^+ > K^+$



Temperature Dependence of Moduli

As temperature is increased

- Glass network softens
- Atoms and ions of the network begin to flow
- At Tg, the glass becomes a supercooled liquid
- Liquid supports no stress
- Modulus falls to zero
- Behavior now characterized as a viscous liquid
- The higher the Tg, the higher the temperature before softening
- The lower the Tg, the lower the temperature before softening



Soda lime silicate glass