CERAMICS: CHAPTERS 12&13

ISSUES TO ADDRESS...

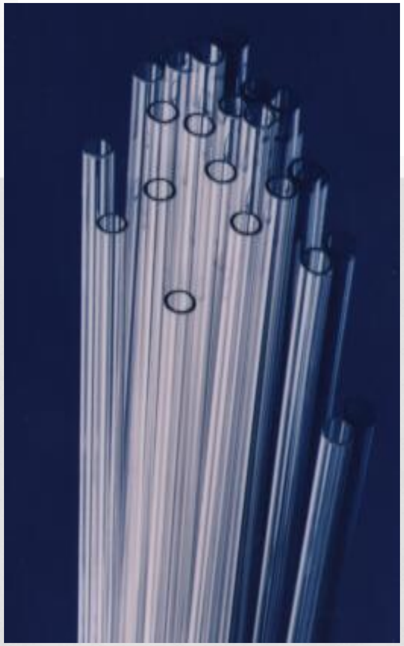
- **Definitions and Classification**
- **Structures of ceramic materials:**
  How do they differ from that of metals?
- **Point defects:**
  How are they different from those in metals?
- **Impurities:**
  How are they accommodated in the lattice and how do they affect properties?
- **Mechanical Properties:**
  What special provisions/tests are made for ceramic materials?

CERAMICS: DEFINTIONS (1)

- The word "ceramics" comes from the Greek word "**Keramos**" meaning "Pottery," "Potter's Clay," or "a Potter." This Greek word is related to an old Sanskrit root meaning "***to burn***" but was primarily used to mean "burnt stuff."

- ***Ceramics*** are defined as products made from inorganic materials having non-metallic properties, usually processed at a high temperature at some time during their manufacture.

GLASS-CERAMICS

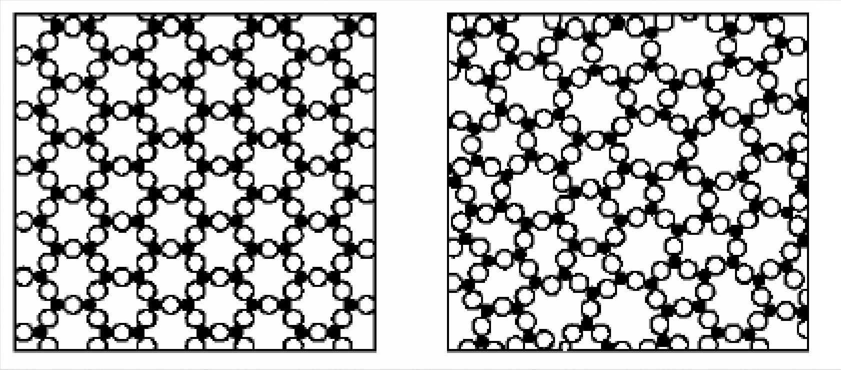


Quartz tubing is fabricated from beach sand

The lamp applications are shown in the GE product montage

Highly thermal resistive ceramics

Ceramics Crystals: *atoms have long range periodic order*



Glasses (non-crystalline) *atoms have short range order only (**amorphous**)*

CERAMICS

Ceramic rotors under commercial production
Materials: Sintered silicon nitride

Common ceramic materials with characteristic resistance to damage at high temperature and corrosive environments

A ceramic turbine in the millimeter range for micro-electromechanical systems, termed MEMS

A prototype ceramic engine

CERAMICS: DEFINTIONS (2)

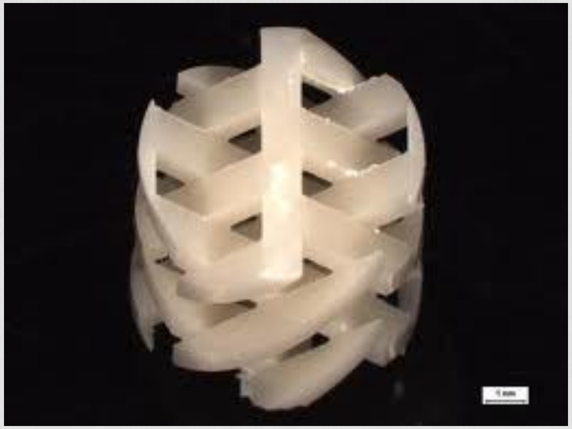
- The ***technical definition*** of ceramics involves a much ***greater variety*** of products than is normally realized. To most people, the word ceramics means dinnerware, figurines, vases, and other objects of ceramic art. The majority of ceramic products not generally recognized.

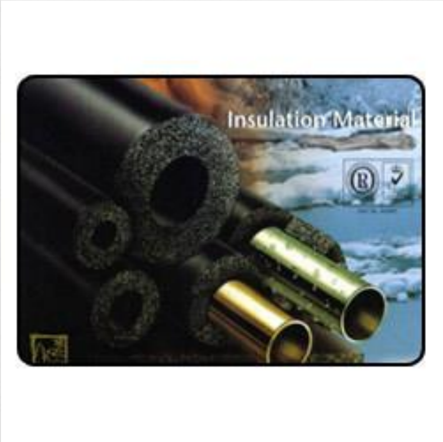
  Examples are bathtubs, washbowls, sinks, electrical insulating devices, water and sewerage pipes, bricks, hollow tile, glazed building tile, floor and wall tile, earthenware, porcelain enamel and glass.

- Ceramic products have a number of outstanding properties which determine their usefulness. One of the most unusual of these is their great durability. This ***durability*** can be divided into three types: ***chemical, mechanical and thermal***.

CERAMICS: PROPERTIES (1)

- **Chemical Durability**
  - The high chemical durability of the great majority of ceramic products makes them *resistant to almost all acids, alkalis, and organic solvents.*
  - Of further importance is the fact that ceramic materials *are not affected by oxygen*. The materials generally contained in the ceramic products have already combined with all of the oxygen for which they have an affinity, and therefore, are not affected further by the presence of oxygen in their environment.





CERAMICS: PROPERTIES (2)

- **Mechanical Durability**

The mechanical durability of ceramics is evidenced by their ***strength and hardness***. The compressive strengths of ceramic materials are extremely high, normally 50,000 to 100,000 lbs/sq. in. The hardness makes ceramic materials very ***resistant to abrasion***. It is this property which makes them useful for floors, and for the grinding of metals and other materials.

CERAMICS: PROPERTIES (3)

- **Thermal Durability**

  Most ceramics have the ability to *withstand high temperatures*. This is why they are useful in the production of all types of heat-containing equipment such as kilns for the ceramic industry, and such products as the inner linings of fireplaces and home heating furnaces.

CLASSIFICATION

- **Technical Ceramics** can also be classified into *three* distinct material *categories*:

Oxides-based: Silicate and non-silicate oxide ceramics (alumina,zirconia, etc)

Non-oxides: Carbides, borides, nitrides, silicides

Composites: Particulate reinforced, combinations of oxides/non-oxides.

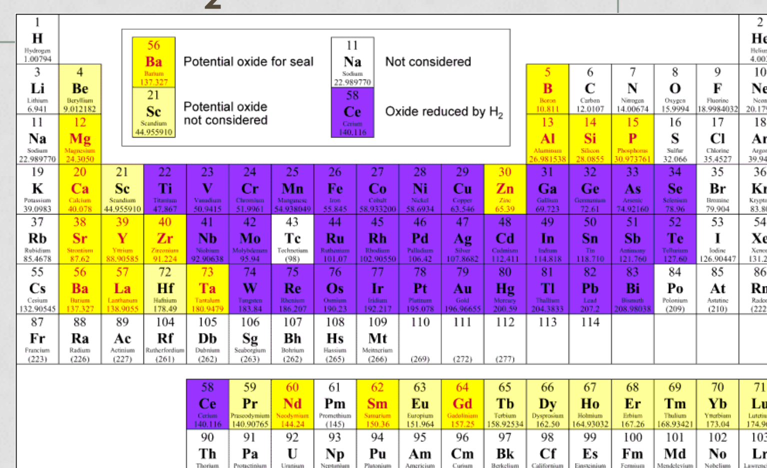
OXIDE CERAMICS

Properties:

- oxidation resistant,
- chemically inert,
- electrically insulating
- generally low thermal conductivity,

Notes:

- relatively simple manufacturing and low cost for Al_2O_3
- more complex manufacturing and higher cost for ZrO_2



NON-OXIDE CERAMICS

Properties:

- Low oxidation resistance,
- Extreme hardness,
- Chemically inert,
- High thermal conductivity,
- May be electrically conducting,

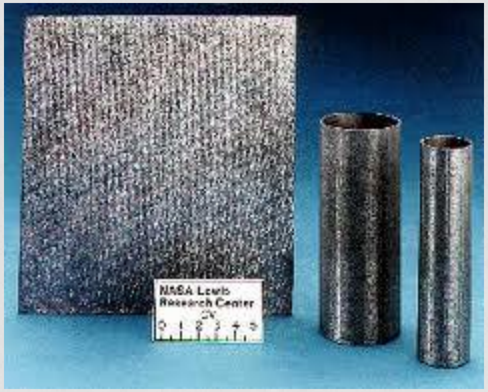
Notes: difficult energy dependent manufacturing and high cost (TiC, ZrN, B_4C, BN, Si_3N_4, SiC etc).

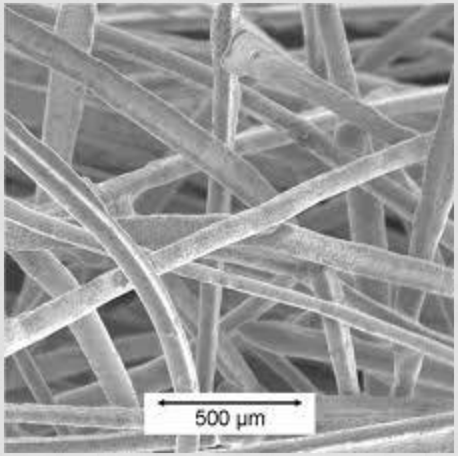
CERAMIC-BASED COMPOSITES

<u>**Properties:**</u>

- Toughness,
- Low and high oxidation resistance (type related),
- Variable thermal and electrical conductivity,

Notes: complex manufacturing processes; high cost



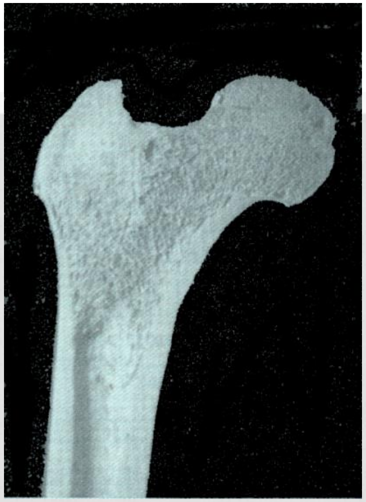


EXAMPLES

Some Silicate Ceramics

Ceramic	Composition (wt %)[a] SiO$_2$	Al$_2$O$_3$	K$_2$O	MgO	CaO	Others
Silica refractory	96					4
Fireclay refractory	50–70	45–25				5
Mullite refractory	28	72				—
Electrical porcelain	61	32	6			1
Steatite porcelain	64	5		30		1
Portland cement	25	9			64	2

[a] These are approximate compositions, indicating primary components. Impurity levels can vary significantly from product to product.



The Body's Ceramic
Hydroxyapatite (HA)
$Ca_{10}(HPO_4)_6(OH)_2$
is the primary mineral content of bone

Some Nonsilicate Oxide Ceramics

Primary composition	Common product names
Al_2O_3	Alumina, alumina refractory
MgO	Magnesia, magnesia refractory, magnesite refractory, periclase refractory
$MgAl_2O_4$ (= MgO · Al_2O_3)	Spinel
BeO	Beryllia
ThO_2	Thoria
UO_2	Uranium dioxide
ZrO_2 (stabilized[b] with CaO)	Stabilized (or partially stabilized) zirconia
$BaTiO_3$	Barium titanate
$NiFe_2O_4$	Nickel ferrite

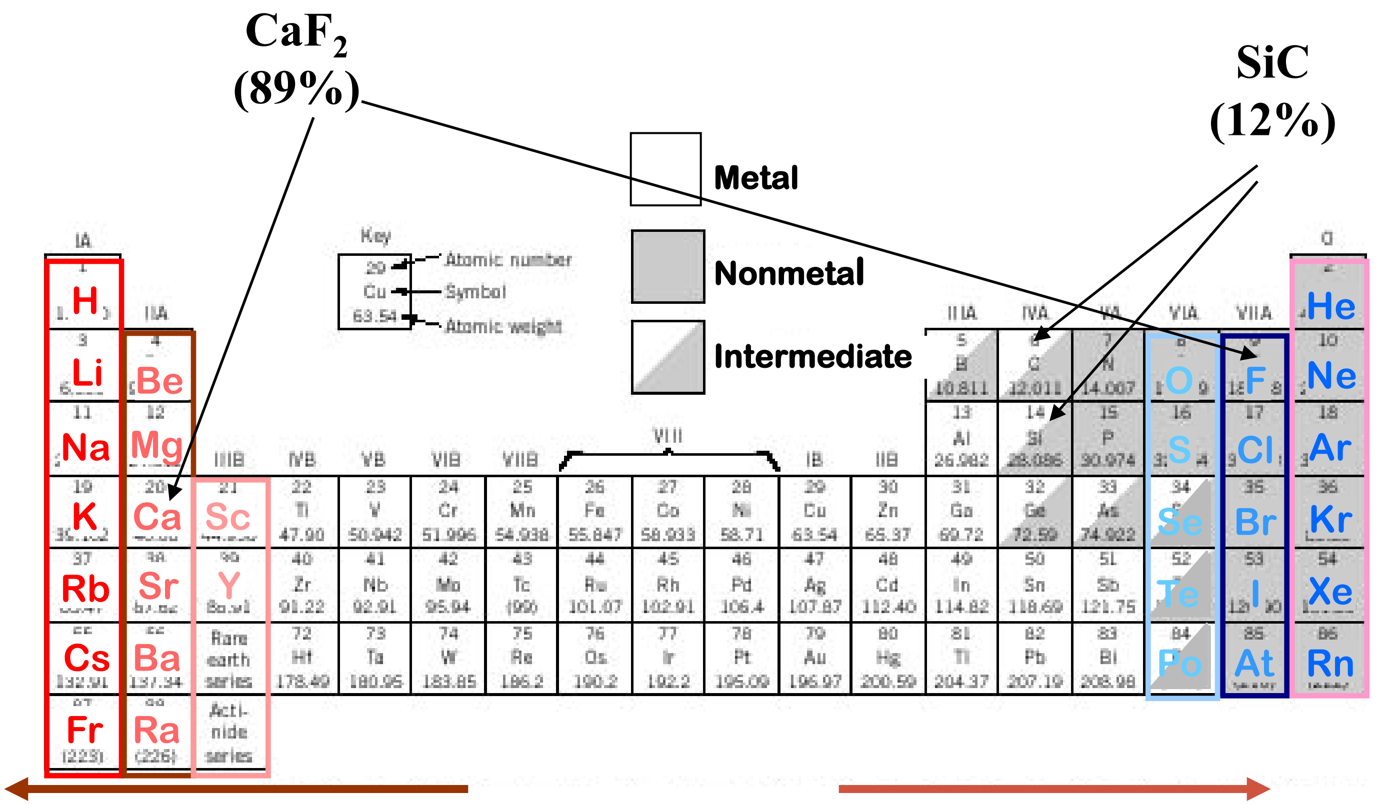
Some Nonoxide Ceramics

Primary composition[a]	Common product names
SiC	Silicon carbide
Si_3N_4	Silicon nitride
TiC	Titanium carbide
TaC	Tantalum carbide
WC	Tungsten carbide
B_4C	Boron carbide
BN	Boron nitride
C	Graphite

[a] Some products may have several weight percent additions or impurities.

CERAMIC BONDING

- **Bonding:**
  - Mostly *ionic*, some covalent.
  - % ionic character increases with difference in electronegativity.



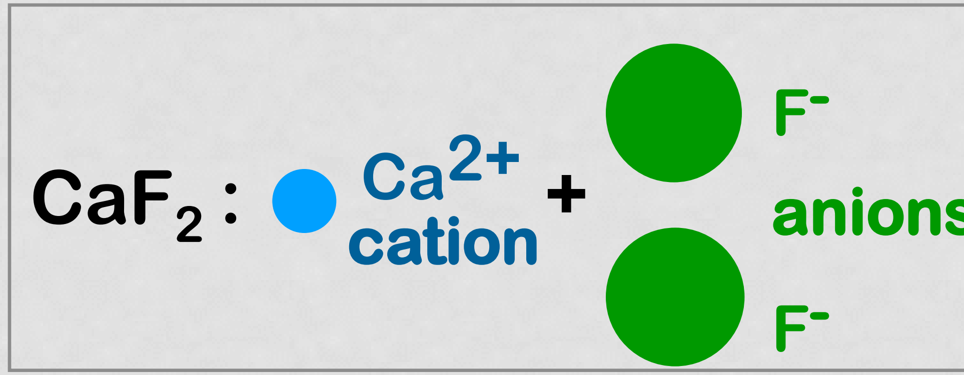
Ceramic	% Ionic Character
CaF_2	89
MgO	73
$NaCl$	67
Al_2O_3	63
SiO_2	51
Si_3N_4	30
ZnS	18
SiC	12

Electropositive elements: Readily give up electrons to become + ions.

Electronegative elements: Readily acquire electrons to become - ions.

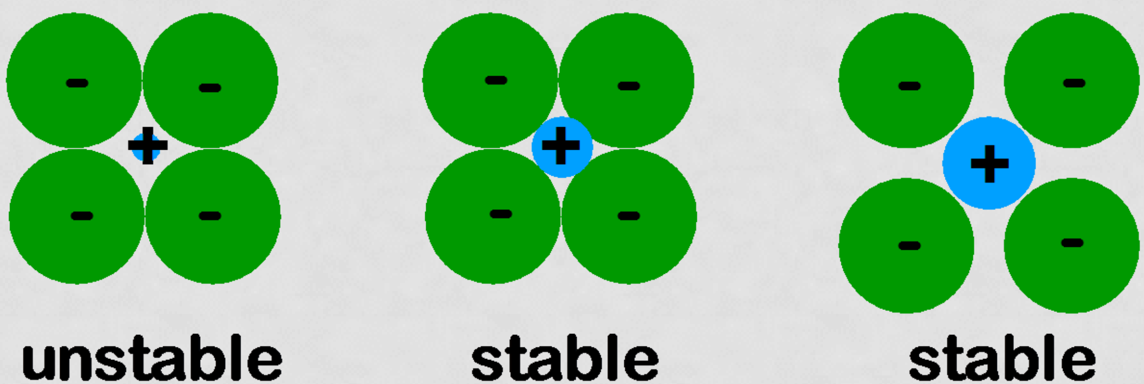
IONIC BONDING & STRUCTURE

- **Charge Neutrality**:
  - Net charge in the structure should be zero.



- **General form:** A_mX_p m, p determined by charge neutrality

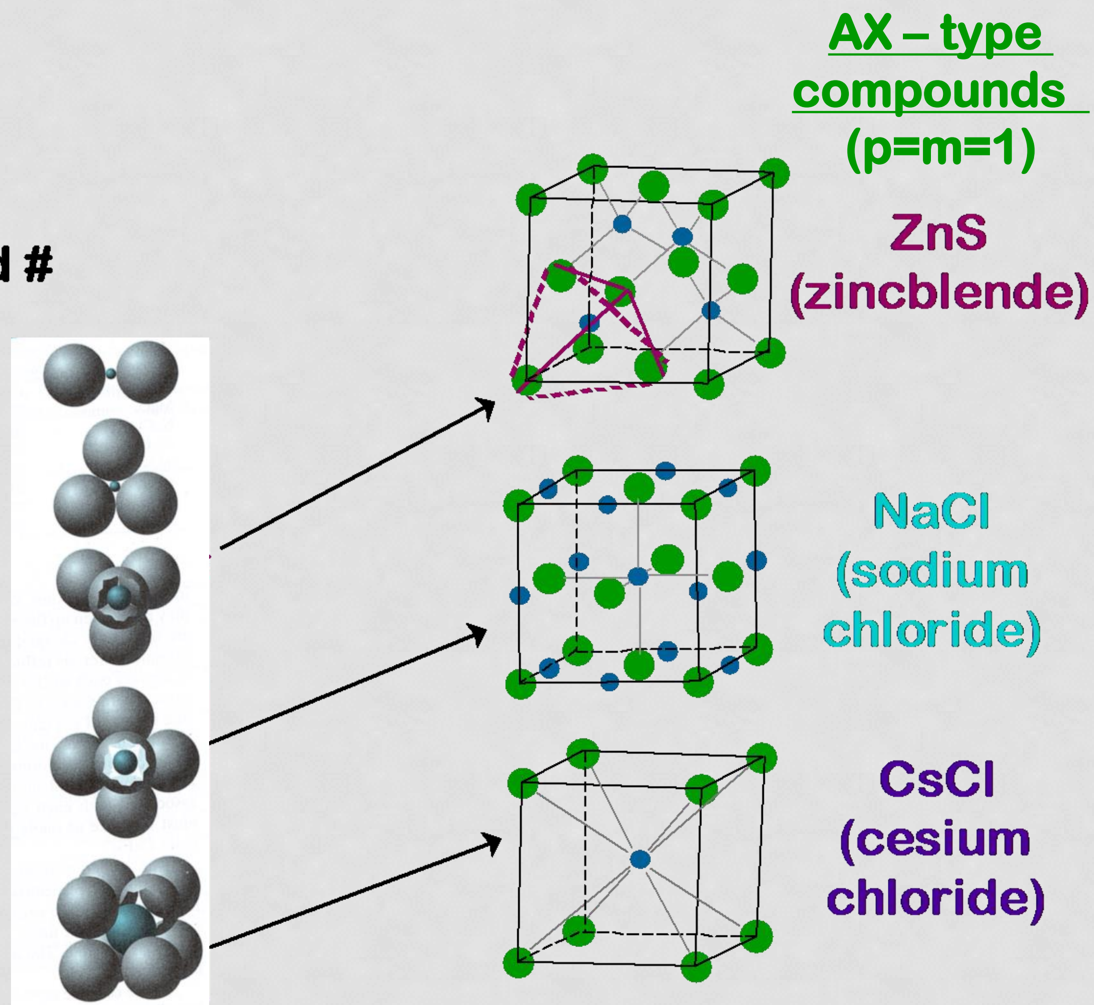
- **Stable crystal structures**: ***maximize*** the # of nearest oppositely charged neighbors, when all anions **are in contact** with that cation, i.e. special relations between cation (r_C) and anion (r_A) radius should hold.



COORDINATION NUMBER

- The ***coordination number*** is a number of anions nearest neighbors for a cation.
- Coordination number increases with ***increasing r_C/r_A ratio***

$\frac{r_{cation}}{r_{anion}}$	Coord #
< .155	2
.155-.225	3
.225-.414	4
.414-.732	6
.732-1.0	8



EXAMPLE: PREDICTION STRUCTURE OF FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100
Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- **Answer:**

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140} = 0.550$$

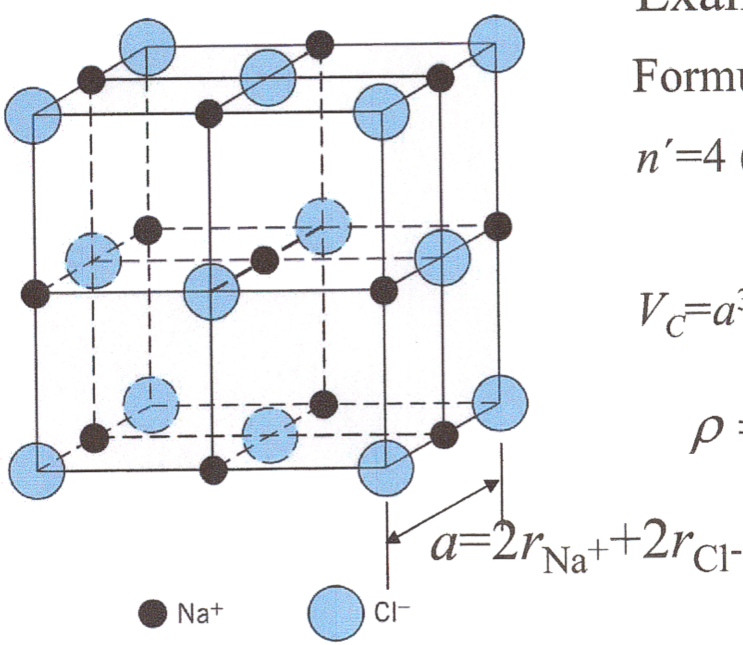
based on this ratio:
-coord # = 6
-structure = NaCl-type

CERAMIC DENSITY COMPUTATION

Number of formula units within the unit cell

$$\rho = \frac{n'(\sum A_C + \sum A_A)}{V_C N_A}$$

Sum of the atomic weights of all anions in the formula unit



Example: density of Sodium Chloride

Formula is NaCl

n'=4 (because there are 4 Na atoms and 4 Cl atoms within a unit cell)

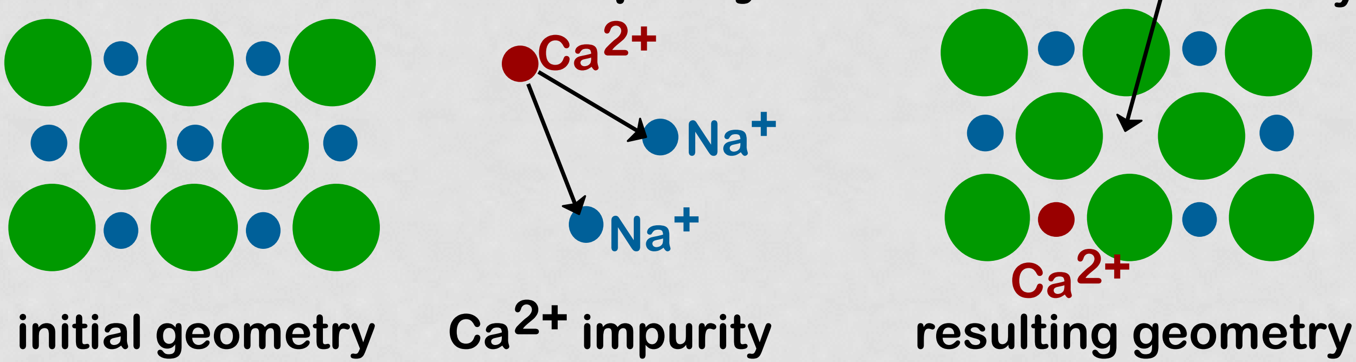
$V_C = a^3 = (2(0.102E\text{-}7) + 2(0.181E\text{-}7))^3 = (0.566E\text{-}7)^3$

$$\rho = \frac{4(22.99 + 35.45)}{(0.566E-7)^3 (6.023E23)} = 2.14 g/cm^3$$

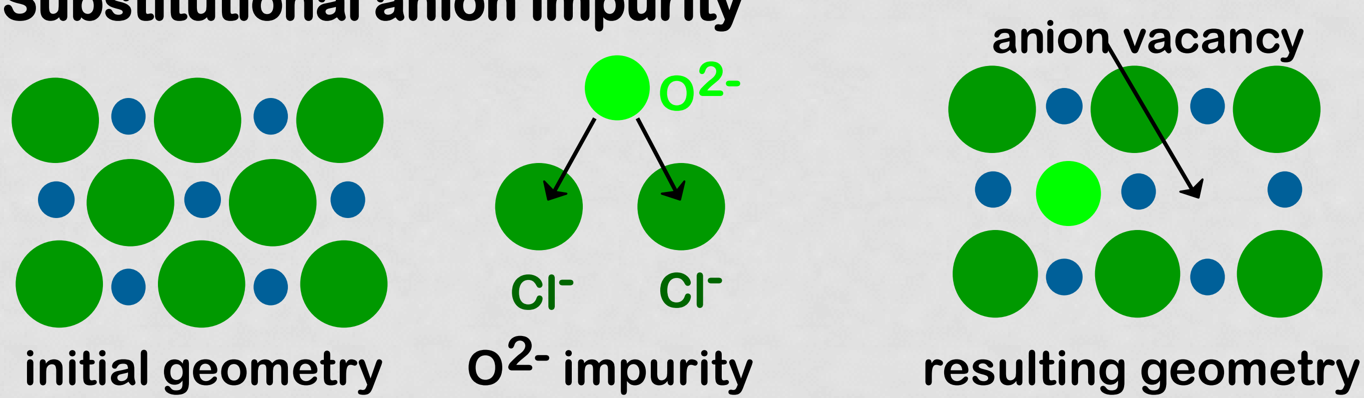
IMPURITIES IN CERAMICS

- **Impurities must also satisfy charge balance**
- Ex: NaCl

- **Substitutional cation impurity**



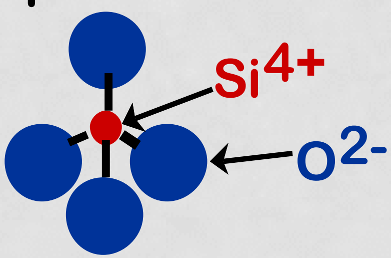
- **Substitutional anion impurity**



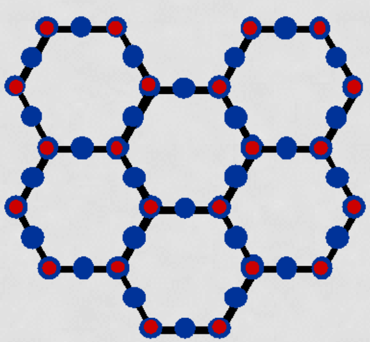
GLASS STRUCTURE

- Basic Unit:

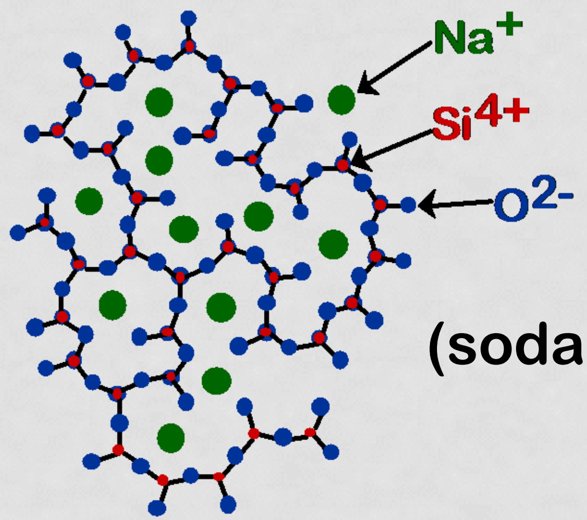
SiO_4^{4-} tetrahedron



- Quartz is crystalline SiO_2:



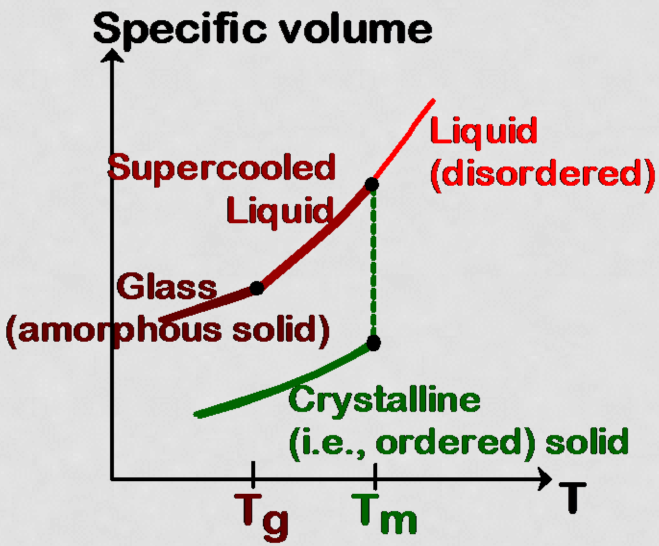
- Glass is amorphous
- Amorphous structure occurs by adding impurities (Na^{+},Mg^{2+},Ca^{2+}, Al^{3+})
- Impurities: interfere with formation of crystalline structure.



(soda glass)

GLASS PROPERTIES

- **Specific volume** (1/ρ) vs Temperature (T):

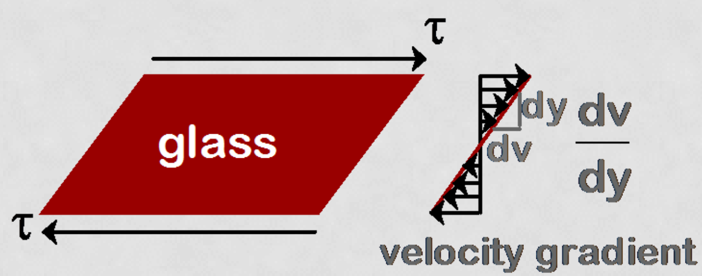


- **Crystalline materials**:
  --crystallize at melting temp, T_m
  --have abrupt change in spec. vol. at T_m

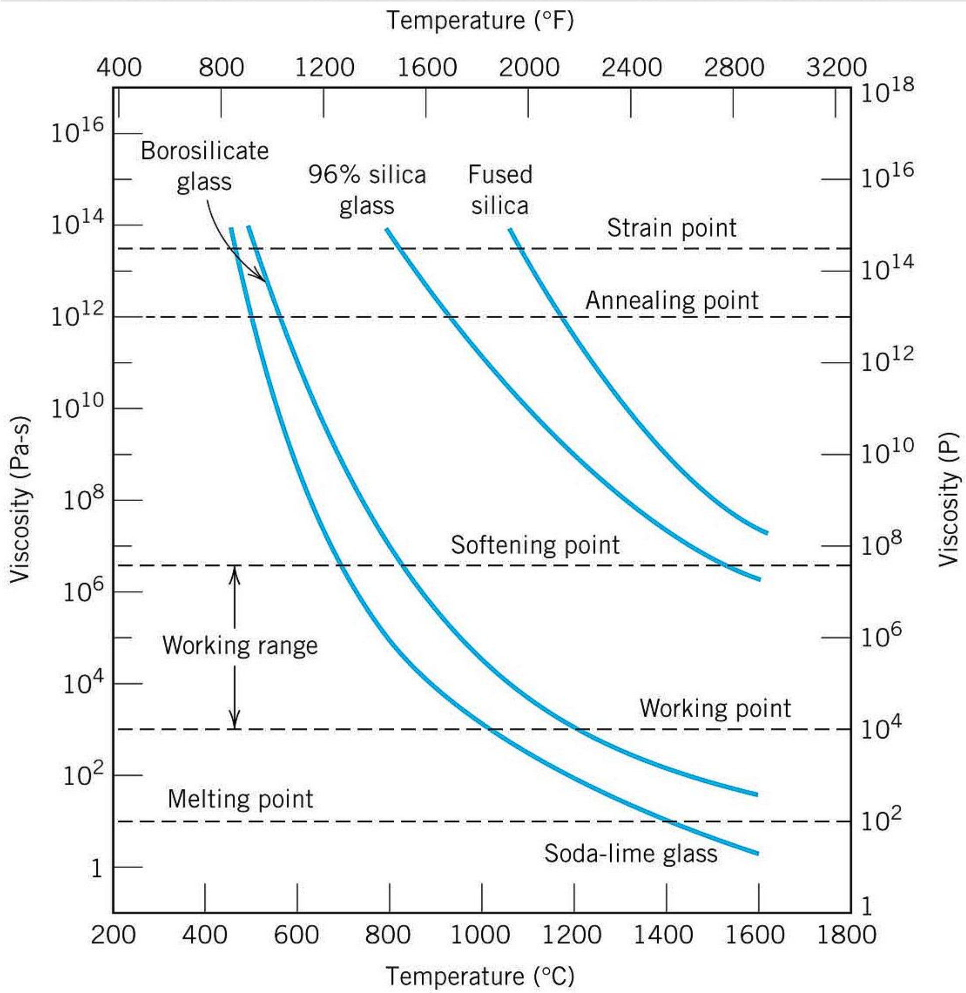
- **Glasses**:
  --do not crystallize
  --spec. vol. varies smoothly with T
  --Glass transition temp, T_g

- **Viscosity**:
  --relates shear stress & velocity gradient:
  --has units of (Pa-s)

$$\tau = \eta \frac{dv}{dy}$$



GLASS VISCOSITY VS TEMPERATURE



- **Viscosity decreases with T**
- **Impurities lower T_{deform}**

Important temperatures in glasses are defined in terms of viscosity

- **Melting point**: viscosity <10^2 P-s, above this temperature glass is liquid
- **Working point**: viscosity ~ 10^3 P-s, glass is easily deformed
- **Softening point**: viscosity = $6x10^6$ P-s, maximum T at which a glass piece maintains shape for a long time
- **Annealing point**: viscosity = 10^{12} P-s, relax internal stresses (diffusion)
- **Strain point**: viscosity = $5x10^{13}$ P-s, above this viscosity, fracture occurs before plastic deformation

Glass forming operations - between softening and working points

VISCOSITY-TEMPERATURE CHARACTERISTICS

Important temperatures in glasses are defined in terms of viscosity

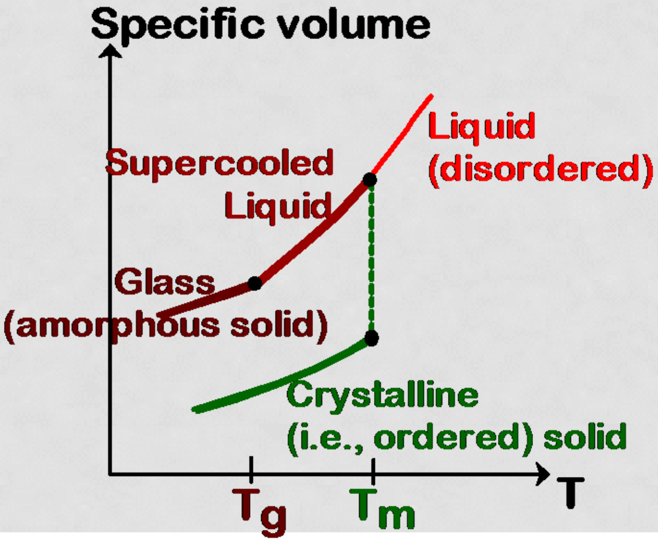
- **Melting point**: viscosity = 100 P, above this temperature glass is liquid
- **Working point**: viscosity = 10^4 P, glass is easily deformed
- **Softening point**: viscosity = 4×10^7 P, maximum T at which a glass piece maintains shape for a long time
- **Annealing point**: viscosity = 10^{13} P, relax internal stresses (diffusion)
- **Strain point**: viscosity = 3×10^{14} P, above this viscosity, fracture occurs before plastic deformation

Glass forming operations - between softening and working points
and working points

TO REMEMBER

The **glass transition temperature** is, for a noncrystalline ceramic, that temperature at which there is a change of slope for the specific volume versus temperature curve .

The **melting temperature** is, for a crystalline material, that temperature at which there is a sudden and discontinuous decrease in the specific volume versus temperature curve.



MECHANICAL PROPERTIRES

MECHANICAL PROPERTIRES: BRITTLE FRACTURE

- In solids with ionic-type bonds, slip (dislocation motion) is difficult because ions of like charge must be brought into close proximity which forms a large barrier for dislocation motion.
- Similarly, in **ceramics** with covalent bonding, slip is not easy (covalent bonds are strong).
- Thus at room temperature ceramics fracture before any plastic deformation occurs – ***brittle fracture***
- The mechanism of brittle structure involves the formation and propagation of ***cracks***
- The measure of a ceramic's ability to resist fracture when a crack is present is the ***fracture toughness***.
- For example a plane strain fracture toughness equals:

- $K_{ic} = Y\sigma(\pi a)^{0.5}$

Y -dimensionless parameter, which depends on sample geometry; **a -**crack's half length.

•**Non-crystalline ceramics:** there is no regular crystalline structure, thus no dislocations. Materials deform by ***viscous flow***, i.e. by breaking and reforming atomic bonds, allowing ions/atoms to slide past each other (like in a liquid).

•***Viscosity*** is a measure of glassy material's resistance to deformation.

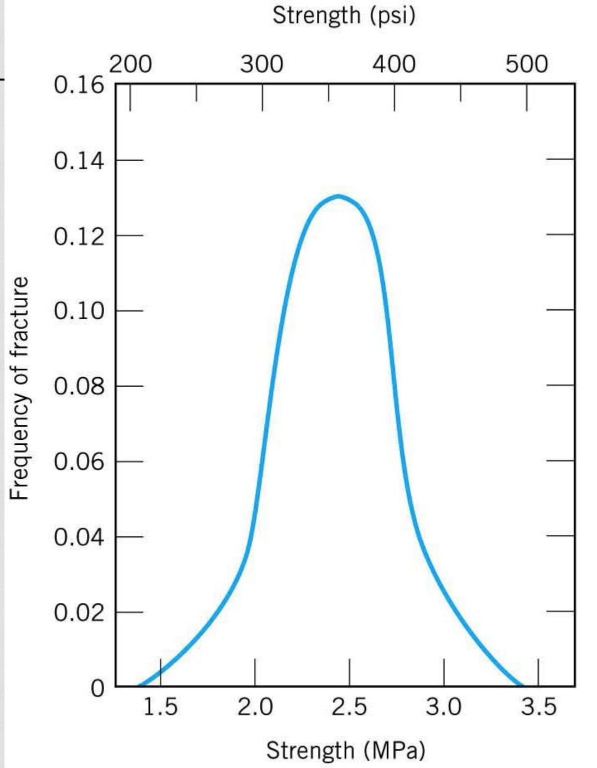
WEIBULL MODULUS

- It appears that for brittle materials (e.g. ceramics) the maximum stress that they can withstand, **varies unpredictably** from specimen to specimen even under **identical testing conditions**
- Thus the strength of brittle material is not a well define value and has to be described with respect to **fracture statistics**

•A Weibull distribution of strength with a flexible two-parameter analytic formula has been found to describe a brittle body fracture. The probability (P) of failure for a brittle material is given by:

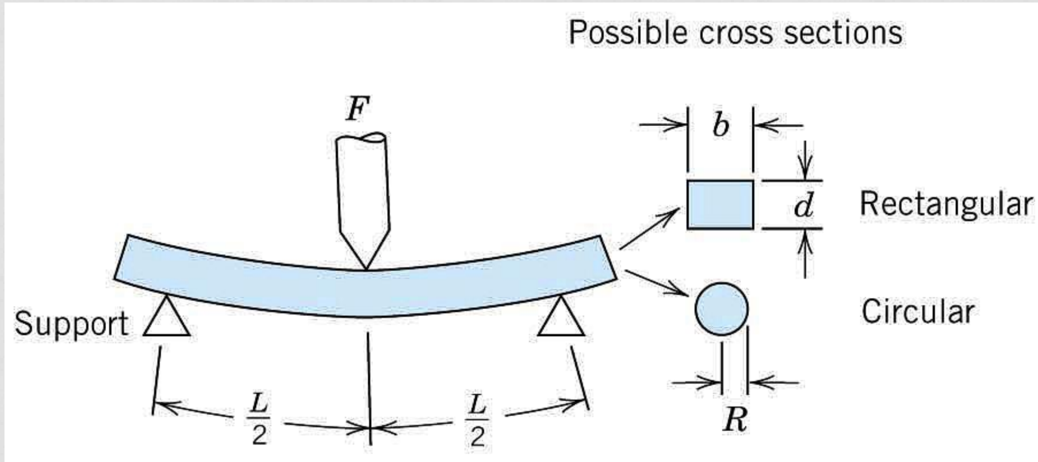
$$\mathbf{P(\sigma) = 1\text{-}exp(-[\sigma/\sigma_o]^m)}$$

where σ-a failure strength, σ_o - a scaling constant and **m** is a the **Weibull modulus** that is a measure of a degree of **strength dispersion**



MEASURING STRENGTH

- A **three-point bend test** to measure the flexural strength, σ_{fs}



$$\sigma = \text{stress} = \frac{Mc}{I}$$

where M = maximum bending moment
c = distance from center of specimen to outer fibers
I = moment of inertia of cross section
F = applied load

	M	c	I	σ
Rectangular	$\frac{FL}{4}$	$\frac{d}{2}$	$\frac{bd^3}{12}$	$\frac{3FL}{2bd^2}$
Circular	$\frac{FL}{4}$	R	$\frac{\pi R^4}{4}$	$\frac{FL}{\pi R^3}$

Typical values for different ceramics

Material	σ_{fs}(MPa)	E(GPa)
Si nitride	700-1000	300
Si carbide	550-860	430
Al oxide	275-550	390
glass (soda)	69	69

SUMMARY

- Ceramic materials have mostly covalent & some ionic bonding.
- Structures are based on:
  --charge neutrality
  --maximizing # of nearest oppositely charged neighbors.
- Structures may be predicted based on:
  --ratio of the cation and anion radii.
- Defects
  --must preserve charge neutrality
  --have a concentration that varies exponentially w/T.
- Room T mechanical response is elastic, but fracture brittle, with negligible ductility.
- Elevated T creep properties are generally superior to those of metals (and polymers).

TAXONOMY OF CERAMICS

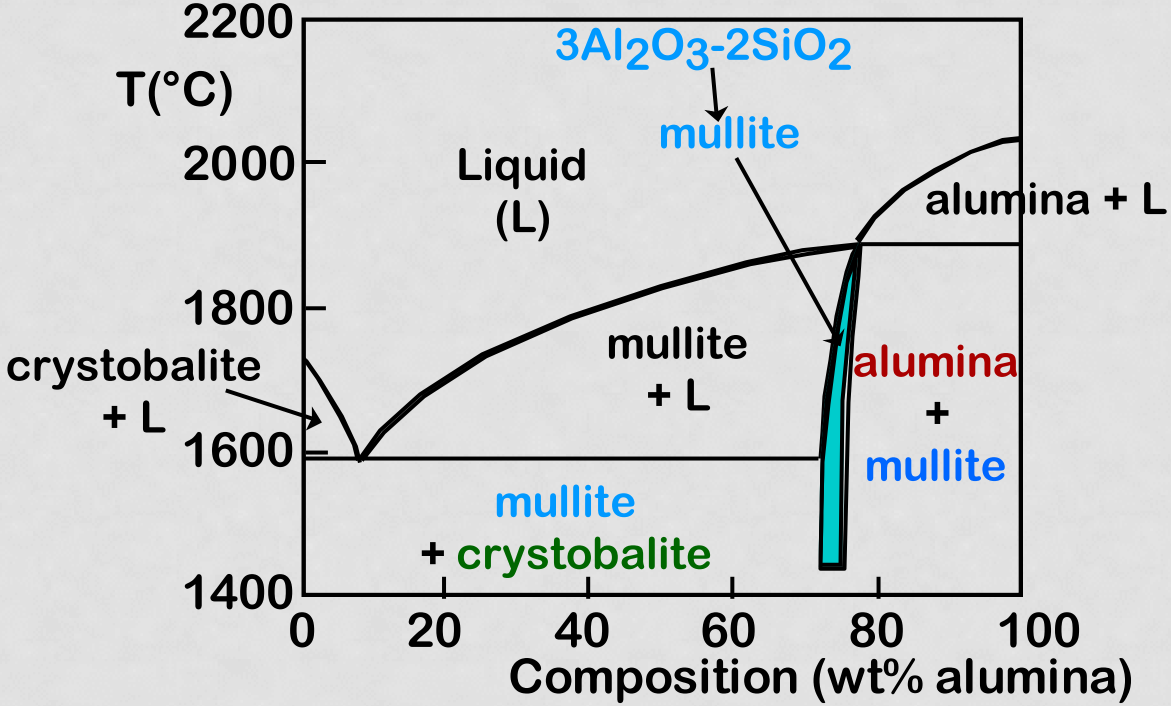
- Glasses
  - -optical
  - -composite reinforce
  - -containers/
  - -household
- Clay products
  - -whiteware
  - -bricks
- Refractories
  - -bricks for high T (furnaces)
- Abrasives
  - -sandpaper
  - -cutting
  - -polishing
- Cements
  - -composites
  - -structural
- Advanced ceramics
  - engine
    - -rotors
    - -valves
    - -bearings
  - -sensors

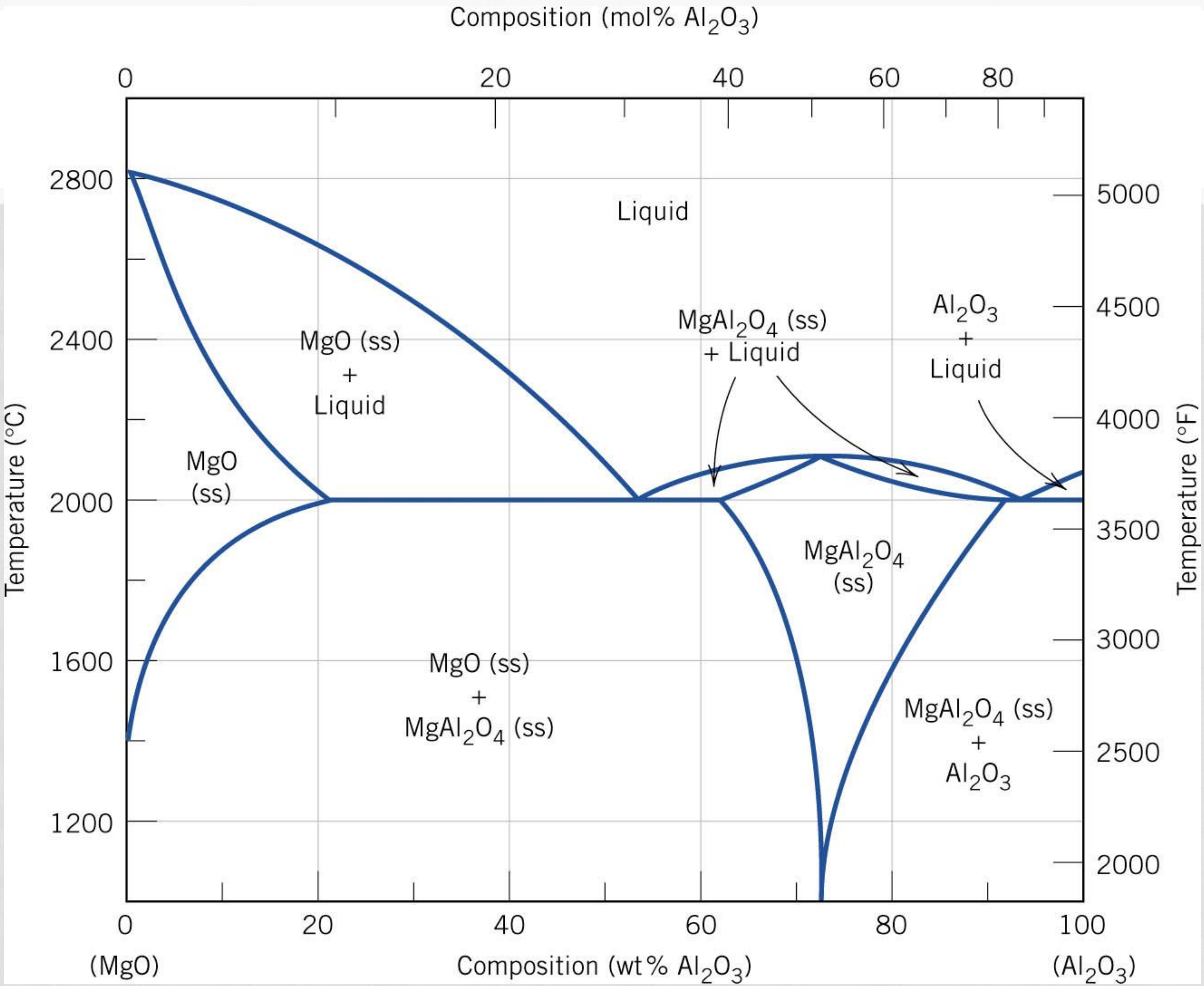
- Properties:
  --T_{melt} for glass is moderate, but large for other ceramics.
  --Small toughness, ductility; large moduli & creep resist.
- Applications:
  --High T, wear resistant, novel uses from charge neutrality.
- Fabrication
  --some glasses can be easily formed
  --other ceramics can not be formed or cast.

APPLICATION: REFRACTORIES

- Need a material to use in high temperature furnaces.
- Consider Silica (SiO_2) - Alumina (Al_2O_3) system.
- Phase diagram shows:

mullite, alumina, and crystobalite (made up of SiO_2) tetrahedra as candidate refractories.

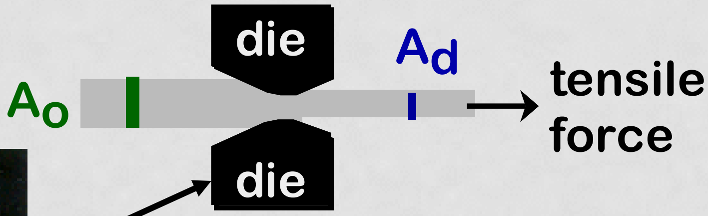


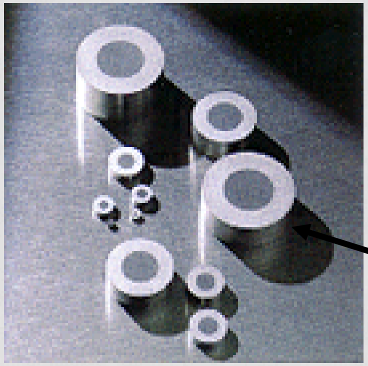


Composition (mol% Al2O3)
0
20
40
60
80
2800
2400
2000
1600
1200
5000
4500
4000
3500
3000
2500
2000
Liquid
MgO (ss) + Liquid
MgAl2O4 (ss) + Liquid
Al2O3 + Liquid
MgO (ss)
MgAl2O4 (ss)
MgO (ss) + MgAl2O4 (ss)
MgAl2O4 (ss) + Al2O3
Temperature (°C)
Temperature (°F)
0
20
40
60
80
100
(MgO)
Composition (wt% Al2O3)
(Al2O3)

APPLICATION: DIE BLANKS

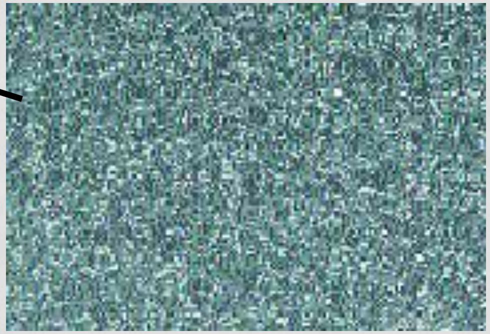
- **Die blanks:**
  --Need wear resistant properties!





Courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

- **Die surface:**
  --4 μm polycrystalline diamond particles that are sintered on to a cemented tungsten carbide substrate.
  --polycrystalline diamond helps control fracture and gives uniform hardness in all directions.



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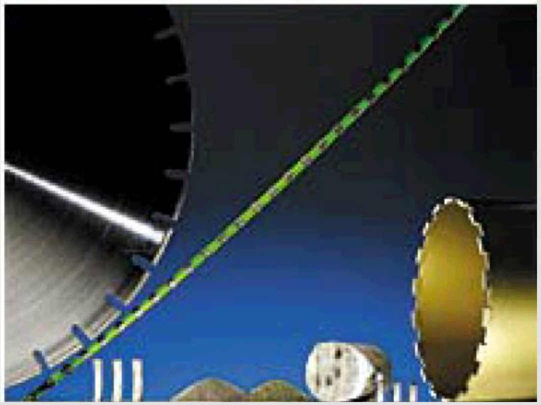
APPLICATION: CUTTING TOOLS

- **Tools:**
  --for grinding glass, tungsten, carbide, ceramics
  --for cutting Si wafers
  --for oil drilling

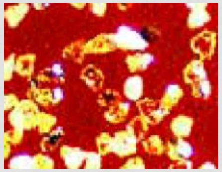
- **Solutions:**
  --manufactured single crystal or polycrystalline diamonds in a metal or resin matrix.
  --optional coatings (e.g., Ti to help diamonds bond to a Co matrix via alloying)
  --polycrystalline diamonds resharpen by microfracturing along crystalline planes.

oil drill bits



blades

coated single crystal diamonds

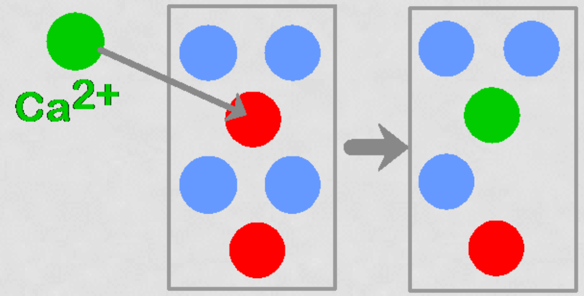


polycrystalline diamonds in a resin matrix.

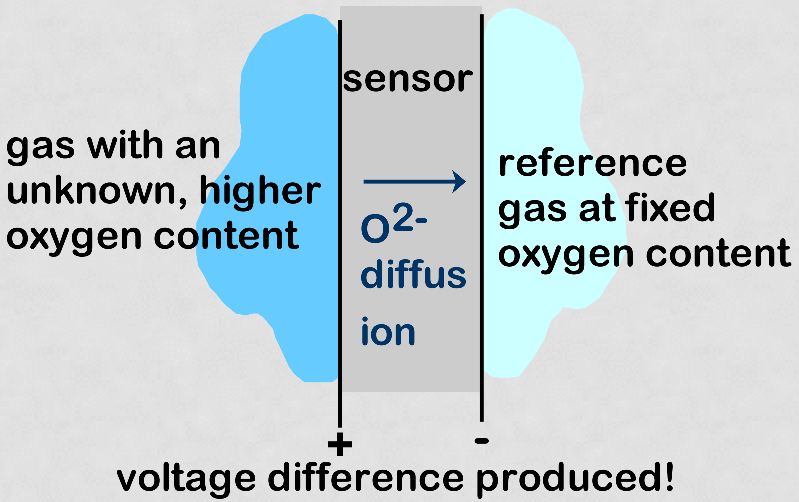
Photos courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.

APPLICATION: SENSORS

- Ex: Oxygen sensor: ZrO_2
- Principle: Make diffusion of ions fast for rapid response.
- Approach:
  Add Ca impurity to:
  --increase O^{2-} vacancies
  --increase O^{2-} diffusion
- Operation:
  --voltage difference produced when O^{2-} ions diffuse between external and references gases.



A Ca^{2+} impurity removes a Zr^{4+} and a O^{2-} ion.



SUMMARY

- Basic categories of ceramics:
  --glasses
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  --refractories
  --cements
  --advanced ceramics
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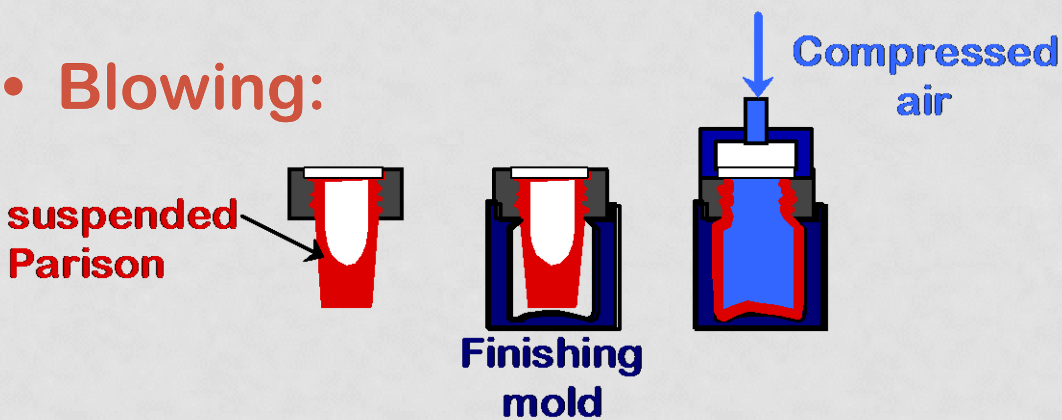
CERAMIC FABRICATION METHODS-I

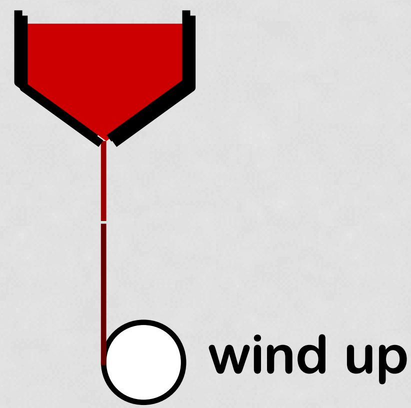
GLASS FORMING | PARTICULATE FORMING | CEMENTATION

- Pressing:

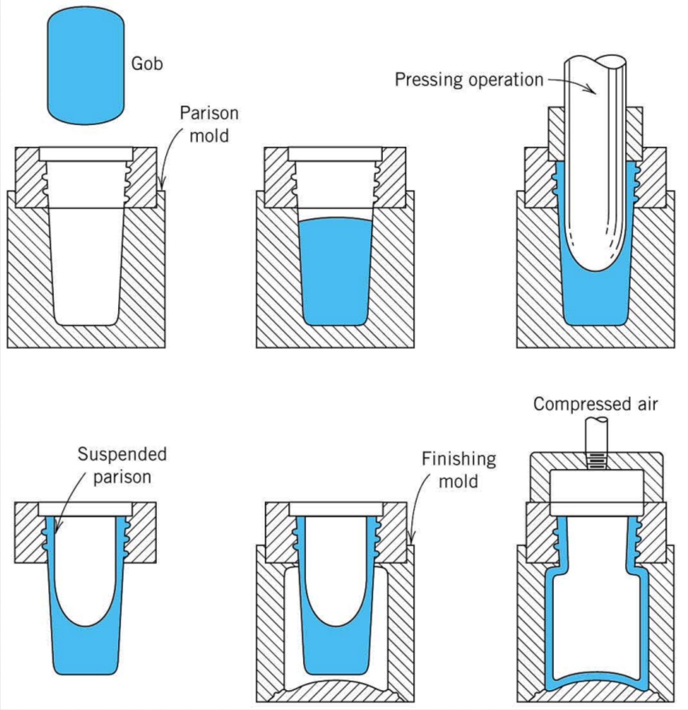
- Blowing:



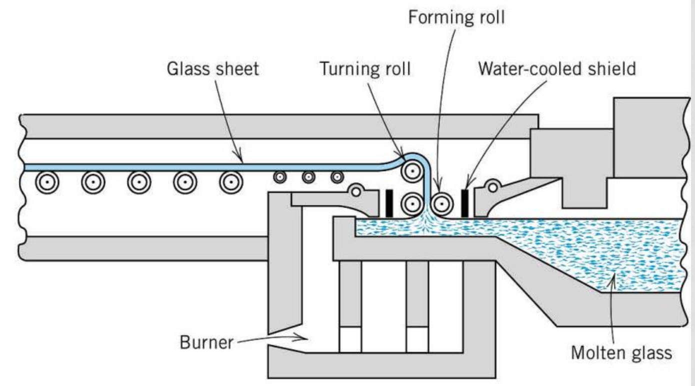
- Fiber drawing:



GLASS FORMING



The press – and –blow technique
for glass bottle production



Continuous drawing of sheet glass

Hot-rolling!

THERMAL STRESSES

- **Residual thermal stresses** are introduced into a glass piece when it is cooled because surface and interior regions cool at different rates, and, therefore, contract different amounts; since the material will experience very little, if any deformation, stresses are established.

- The thinner the thickness of a glass ware the smaller the thermal stresses that are introduced when it is either heated or cooled. The reason for this is that the difference in temperature across the cross-section of the ware, and, therefore, the difference in the degree of expansion or contraction will decrease with a decrease in thickness.

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.

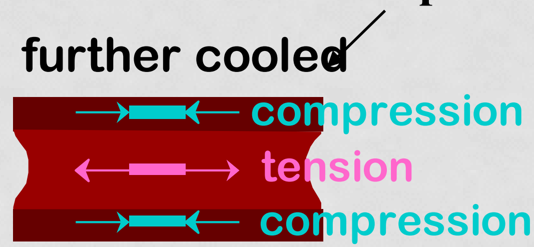
  --sequence:

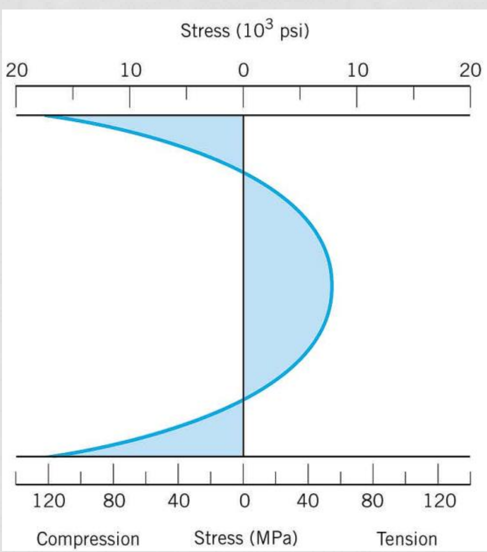
before cooling

surface cooling

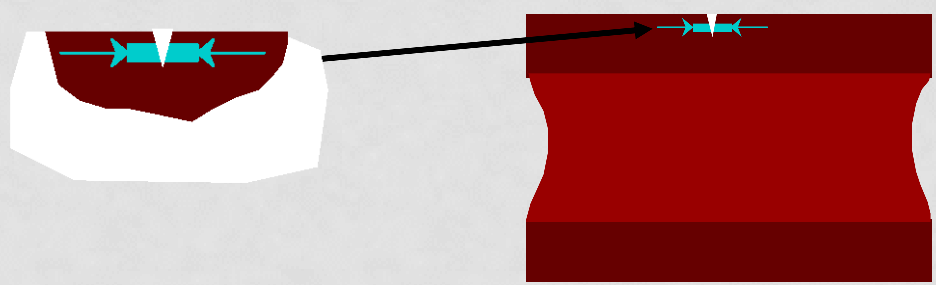
further cooled

Tempered glass





--Result: surface crack growth is suppressed

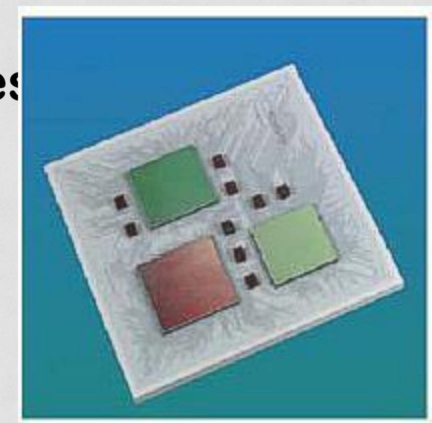


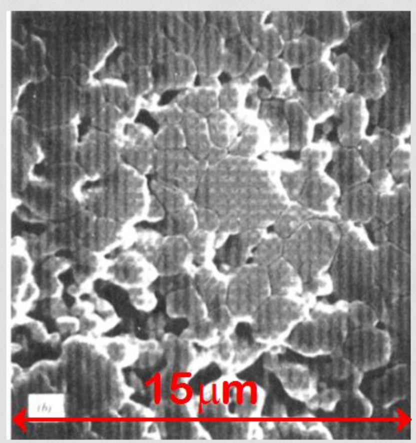
- The strength is enhanced !!

CERAMIC FABRICATION METHODS-IIB

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

- Sintering: useful for both clay and non-clay compositions.
- **Procedure:**
  --grind to produce ceramic and/or glass particles
  --inject into mold
  --press at elevated T to reduce pore size.
- **Aluminum oxide powder:**
  --sintered at 1700C
  for 6 minutes.


Multichip module in alumina ceramic with flip-chip decoupling capacitors

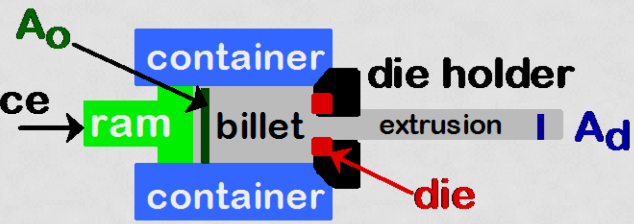


CERAMIC FABRICATION METHODS-IIA

GLASS FORMING | **PARTICULATE FORMING** | CEMENTATION

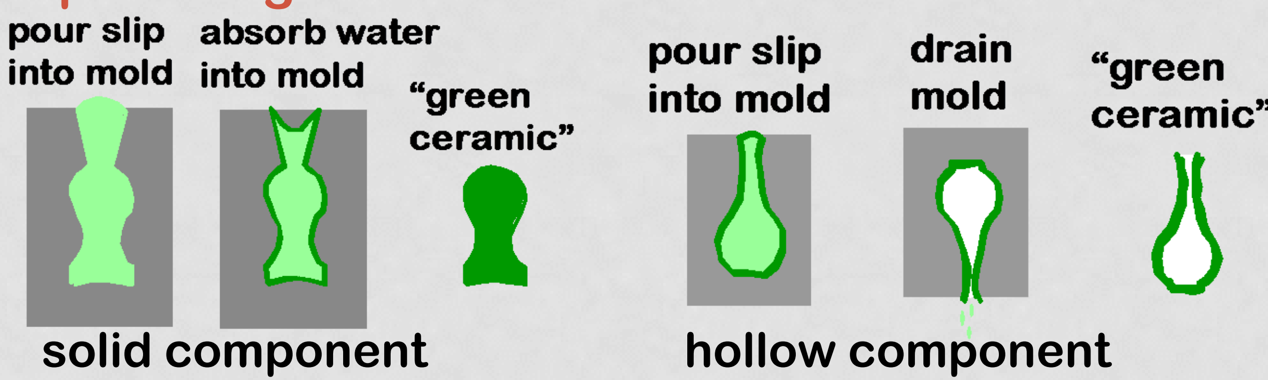
- Milling and screening: desired particle size
- Mixing particles & water: produces a "slip" – highly plastic media
- Form a "green" component

--Hydroplastic forming:
extrude the slip (e.g., into a pipe)



pacificator

--Slip casting:



- Dry and Fire the component

Clay Products

CERAMIC FABRICATION METHODS-III

GLASS FORMING | PARTICULATE FORMING | **CEMENTATION**

- Produced in extremely large quantities.
- Portland cement:
  - --mix clay and lime bearing materials
  - --calcinate (heat to 1400C)
  - --primary constituents:
    - tri-calcium silicate
    - di-calcium silicate
- Adding water
  - --produces a paste which hardens
  - --hardening occurs due to hydration (chemical reactions with the water).
- Forming: done usually minutes after hydration begins.

Example of hydration reaction:

$$2CaO\text{-}SiO_2 + xH_2O = 2CaO\text{-}SiO_2\text{-}xH_2O$$

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