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?
• 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.
Quartz tubing is fabricated from beach sand

The lamp applications are shown in the GE product montage

Ceramics Crystals:
- atoms have long range periodic order

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

Highly thermal resistive ceramics

High temperature (the torch flame)

Low temperature (the ice cube)
CERAMICS

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
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.
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.
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 $\text{Al}_2\text{O}_3$
- more complex manufacturing and higher cost for $\text{ZrO}_2$
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, B₄C, BN, Si₃N₄, SiC etc).
CERAMIC-BASED COMPOSITES

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

Notes: complex manufacturing processes; high cost
EXAMPLES

Some Silicate Ceramics

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>K₂O</th>
<th>MgO</th>
<th>CaO</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica refractory</td>
<td>96</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4</td>
</tr>
<tr>
<td>Fireclay refractory</td>
<td>50–70</td>
<td>45–25</td>
<td></td>
<td></td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>Mullite refractory</td>
<td>28</td>
<td>72</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrical porcelain</td>
<td>61</td>
<td>32</td>
<td>6</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Steatite porcelain</td>
<td>64</td>
<td>5</td>
<td>30</td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Portland cement</td>
<td>25</td>
<td>9</td>
<td></td>
<td>64</td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

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

The Body’s Ceramic

Hydroxyapatite (HA) $\text{Ca}_{10}(\text{HPO}_4)_6(\text{OH})_2$ is the primary mineral content of bone.

Some Nonsilicate Oxide Ceramics

<table>
<thead>
<tr>
<th>Primary composition</th>
<th>Common product names</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Alumina, alumina refractory</td>
</tr>
<tr>
<td>MgO</td>
<td>Magnesia, magnesia refractory, magnesite refractory, periclase refractory</td>
</tr>
<tr>
<td>MgAl₂O₄ (₉ MgO . Al₂O₃)</td>
<td>Spinel</td>
</tr>
<tr>
<td>BeO</td>
<td>Beryllia</td>
</tr>
<tr>
<td>ThO₂</td>
<td>Thoria</td>
</tr>
<tr>
<td>UO₂</td>
<td>Uranium dioxide</td>
</tr>
<tr>
<td>ZrO₂ (stabilized b with CaO)</td>
<td>Stabilized (or partially stabilized) zirconia</td>
</tr>
<tr>
<td>BaTiO₃</td>
<td>Barium titanate</td>
</tr>
<tr>
<td>NiFe₂O₄</td>
<td>Nickel ferrite</td>
</tr>
</tbody>
</table>

Some Nonoxide Ceramics

<table>
<thead>
<tr>
<th>Primary composition</th>
<th>Common product names</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>Silicon carbide</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>Silicon nitride</td>
</tr>
<tr>
<td>TiC</td>
<td>Titanium carbide</td>
</tr>
<tr>
<td>TaC</td>
<td>Tantalum carbide</td>
</tr>
<tr>
<td>WC</td>
<td>Tungsten carbide</td>
</tr>
<tr>
<td>B₄C</td>
<td>Boron carbide</td>
</tr>
<tr>
<td>BN</td>
<td>Boron nitride</td>
</tr>
<tr>
<td>C</td>
<td>Graphite</td>
</tr>
</tbody>
</table>

*Some products may have several weight percent additions or impurities.*
Electropositive elements:
Readily give up electrons to become + ions.

Electronegative elements:
Readily acquire electrons to become - ions.

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

**CERAMIC BONDING**

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>% Ionic Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaF₂</td>
<td>89</td>
</tr>
<tr>
<td>MgO</td>
<td>73</td>
</tr>
<tr>
<td>NaCl</td>
<td>67</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>63</td>
</tr>
<tr>
<td>SiO₂</td>
<td>51</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>30</td>
</tr>
<tr>
<td>ZnS</td>
<td>18</td>
</tr>
<tr>
<td>SiC</td>
<td>12</td>
</tr>
</tbody>
</table>
 Ionic Bonding & Structure

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

- **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.

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

- **Example**: $CaF_2$: $Ca^{2+}$ cation + $F^-$ anions

Unstable: ![Unstable Structure Image]

Stable: ![Stable Structure Images]
The *coordination number* is a number of anions nearest neighbors for a cation. Coordination number increases with *increasing* $r_c/r_a$ ratio.

<table>
<thead>
<tr>
<th>$r_c/r_a$</th>
<th>Coord #</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; .155</td>
<td>2</td>
</tr>
<tr>
<td>.155-.225</td>
<td>3</td>
</tr>
<tr>
<td>.225-.414</td>
<td>4</td>
</tr>
<tr>
<td>.414-.732</td>
<td>6</td>
</tr>
<tr>
<td>.732-1.0</td>
<td>8</td>
</tr>
</tbody>
</table>
**EXAMPLE: PREDICTION STRUCTURE OF FeO**

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

<table>
<thead>
<tr>
<th>Cation</th>
<th>Ionic radius (nm)</th>
<th>( r_{\text{cation}} )</th>
<th>( r_{\text{anion}} )</th>
<th>Answer:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(^{3+})</td>
<td>0.053</td>
<td>0.077</td>
<td>0.140</td>
<td>0.550</td>
</tr>
<tr>
<td>Fe(^{2+})</td>
<td>0.077</td>
<td>0.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(^{3+})</td>
<td>0.069</td>
<td>0.140</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>0.100</td>
<td>0.140</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- **Anion**

<table>
<thead>
<tr>
<th>Anion</th>
<th>Ionic radius (nm)</th>
<th>( r_{\text{cation}} )</th>
<th>( r_{\text{anion}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^{2-})</td>
<td>0.140</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>0.181</td>
<td>0.140</td>
<td></td>
</tr>
<tr>
<td>F(^{-})</td>
<td>0.133</td>
<td>0.140</td>
<td></td>
</tr>
</tbody>
</table>

- **Answer:**
  - 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

\[ n' = 4 \text{ (because there are 4 Na atoms and 4 Cl atoms within a unit cell)} \]

\[ V_C = a^3 = (2(0.102E-7) + 2(0.181E-7))^3 = (0.566E-7)^3 \]

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

- Impurities must also satisfy **charge balance**
- Ex: NaCl \(\text{Na}^+ \bullet \text{Cl}^-\)
- **Substitutional cation impurity**
  - Initial geometry
  - \(\text{Ca}^{2+}\) impurity
  - Resulting geometry
- **Substitutional anion impurity**
  - Initial geometry
  - \(\text{O}^{2-}\) impurity
  - Resulting geometry
• Basic Unit:
  \[ \text{Si}_4\text{O}_4^{4-} \]

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

• Quartz is crystalline SiO\(_2\):

(soda glass)
GLASS PROPERTIES

- **Specific volume** \(1/\rho\) vs Temperature (T):
  - Glasses: --do not crystallize
    --spec. vol. varies smoothly with T
  - Crystalline materials:
    --crystallize at melting temp, \(T_m\)
    --have abrupt change in spec. vol. at \(T_m\)

- **Glasses:**
  --Glass transition temp, \(T_g\)

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

\[ \tau = \eta \frac{dv}{dy} \]
• Viscosity decreases with $T$
• Impurities lower $T_{\text{deform}}$

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 $\sim 10^3$ P-s, glass is easily deformed

• **Softening point**: viscosity $= 6 \times 10^6$ 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 $= 5 \times 10^{13}$ P-s, above this viscosity, fracture occurs before plastic deformation

Glass forming operations - between softening and working points
Important temperatures in glasses are defined in terms of viscosity:

- **Melting point**: viscosity = $100 \text{ P}$, above this temperature glass is liquid.

- **Working point**: viscosity = $10^4 \text{ P}$, glass is easily deformed.

- **Softening point**: viscosity = $4 \times 10^7 \text{ P}$, maximum temperature at which a glass piece maintains shape for a long time.

- **Annealing point**: viscosity = $10^{13} \text{ P}$, relax internal stresses (diffusion).

- **Strain point**: viscosity = $3 \times 10^{14} \text{ P}$, 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 PROPERTIES
MECHANICAL PROPERTIES: 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:
  \[ K_{ic} = Y \sigma (\pi a)^{0.5} \]

- 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:

\[ P(\sigma) = 1 - \exp\left(-\frac{\sigma}{\sigma_o}\right)^m \]

where \( \sigma \) - a failure strength, \( \sigma_o \) - a scaling constant and \( m \) is 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, $\sigma_{fs}$

**Typical values for different ceramics**

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{fs}$ (MPa)</th>
<th>E (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si nitride</td>
<td>700-1000</td>
<td>300</td>
</tr>
<tr>
<td>Si carbide</td>
<td>550-860</td>
<td>430</td>
</tr>
<tr>
<td>Al oxide</td>
<td>275-550</td>
<td>390</td>
</tr>
<tr>
<td>glass (soda)</td>
<td>69</td>
<td>69</td>
</tr>
</tbody>
</table>
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).
• 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$_2$O$_3$) system.
- Phase diagram shows: mullite, alumina, and crystobalite (made up of SiO$_2$) tetrahedra as candidate refractories.

![Phase diagram of silica-alumina system showing mullite, alumina, and crystobalite phases.](image-url)
APPLICATION: DIE BLANKS

• Die blanks:
  --Need wear resistant properties!

• 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.
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.

Photos courtesy Martin Deakins, GE Superabrasives, Worthington, OH. Used with permission.
**APPLICATION: SENSORS**

- **Ex:** Oxygen sensor: $\text{ZrO}_2$
- **Principle:** Make diffusion of ions fast for rapid response.
- **Approach:**
  - Add Ca impurity to:
    - increase $\text{O}^{2-}$ vacancies
    - increase $\text{O}^{2-}$ diffusion
- **Operation:**
  - voltage difference produced when $\text{O}^{2-}$ ions diffuse between external and references gases.

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

Gas with an unknown, higher oxygen content

Reference gas at fixed oxygen content

Voltage difference produced!
SUMMARY

• Basic categories of ceramics:
  --glasses
  --clay products
  --refractories
  --cements
  --advanced ceramics

• Fabrication Techniques:
  --glass forming (impurities affect forming temp).
  --particulate forming (needed if ductility is limited)
  --cementation (large volume, room T process)

• Heat treating: Used to
  --alleviate residual stress from cooling,
  --produce fracture resistant components by putting surface into compression.
CERAMIC FABRICATION METHODS-I

- Pressing:
  - Gob
  - Parison mold
  - Pressing operation

- Blowing:
  - Suspended Parison
  - Finishing mold
  - Compressed air
  - Wind up

- Fiber drawing:
GLASS FORMING

Continuous drawing of sheet glass
Hot-rolling!

The press – and blow technique for glass bottle production
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
  
<table>
<thead>
<tr>
<th>Hot</th>
<th>Cooler</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hot</td>
<td></td>
</tr>
<tr>
<td>Cooler</td>
<td></td>
</tr>
</tbody>
</table>

--Result: surface crack growth is suppressed

- The strength is enhanced!!
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 1700°C for 6 minutes.
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)

--Slip casting:
pour slip into mold
absorb water into mold
“green ceramic”
pour slip into mold
drain mold
“green ceramic”

solid component
hollow component

Dry and Fire the component
CERAMIC FABRICATION METHODS-III

- Produced in extremely large quantities.
- Portland cement:
  - mix clay and lime bearing materials
  - calcinate (heat to 1400°C)
  - 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:

\[ 2\text{CaO}-\text{SiO}_2+x\text{H}_2\text{O}=2\text{CaO}-\text{SiO}_2-x\text{H}_2\text{O} \]
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