2. ceramics

(1) introduction

- **ceramics** – metallic and nonmetallic elements bounded by ionic and/or covalent bonds
- good electrical and heat insulation property
- brittle, and lesser ductility and toughness than metals
- high chemical stability and high melting temperature
- traditional ceramics: basic components (clay and silica)
- engineering ceramics: pure compounds (Al$_2$O$_3$, SiC)
(2) ceramic crystal structures
(a) ionic and covalent bonding in simple ceramics

**Table 11.1** Some simple ceramic compounds with their melting points

<table>
<thead>
<tr>
<th>Ceramic compound</th>
<th>Formula</th>
<th>Melting point (°C)</th>
<th>Ceramic compound</th>
<th>Formula</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hafnium carbide</td>
<td>HfC</td>
<td>4150</td>
<td>Boron carbide</td>
<td>B₄C₃</td>
<td>2450</td>
</tr>
<tr>
<td>Titanium carbide</td>
<td>TiC</td>
<td>3120</td>
<td>Aluminum oxide</td>
<td>Al₂O₃</td>
<td>2050</td>
</tr>
<tr>
<td>Tungsten carbide</td>
<td>WC</td>
<td>2850</td>
<td>Silicon dioxide†</td>
<td>SiO₂</td>
<td>1715</td>
</tr>
<tr>
<td>Magnesium oxide</td>
<td>MgO</td>
<td>2798</td>
<td>Silicon nitride</td>
<td>Si₃N₄</td>
<td>1700</td>
</tr>
<tr>
<td>Zirconium dioxide</td>
<td>ZrO₂⁺</td>
<td>2750</td>
<td>Titanium dioxide</td>
<td>TiO₂</td>
<td>1605</td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>SiC</td>
<td>2500</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

mixture of ionic and covalent types depends on electronegativity difference

**Table 11.2** Percent ionic and covalent bonding in some ceramic compounds

<table>
<thead>
<tr>
<th>Ceramic compound</th>
<th>Bonding atoms</th>
<th>Electronegativity difference</th>
<th>% ionic character</th>
<th>% covalent character</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zirconium dioxide, ZrO₂</td>
<td>Zr–O</td>
<td>2.3</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>Magnesium oxide, MgO</td>
<td>Mg–O</td>
<td>2.2</td>
<td>69</td>
<td>31</td>
</tr>
<tr>
<td>Aluminum oxide, Al₂O₃</td>
<td>Al–O</td>
<td>2.0</td>
<td>63</td>
<td>37</td>
</tr>
<tr>
<td>Silicon dioxide, SiO₂</td>
<td>Si–O</td>
<td>1.7</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>Silicon nitride, Si₃N₄</td>
<td>Si–N</td>
<td>1.3</td>
<td>34.5</td>
<td>65.5</td>
</tr>
<tr>
<td>Silicon carbide, SiC</td>
<td>Si–C</td>
<td>0.7</td>
<td>11</td>
<td>89</td>
</tr>
</tbody>
</table>
(b) simple ionic arrangements
- packing of ions depends upon
  (i) relative size of ions
  (ii) need to balance electron charges
- if the anion does not touch the cation, then the arrangement is unstable

**Coordination number** – the number of anions that surround a central cation in an ionic solid

**Radius ratio** = \( r_{\text{cation}} / r_{\text{anion}} \)

**Critical radius ratio** for stability

ex. calculate the critical radius \( r/R \) for the triangular coordination (CN = 3)

\[
\cos 30^\circ = \frac{R}{R + r} = 0.866
\]

\[
0.866R + 0.866r = R
\]

\[
0.866r = 0.134R
\]

\[
r/R = 0.134/0.866 = 0.155
\]
ex. predict the coordination number for the ionic solids CsCl and NaCl

for CsCl \( \frac{r(\text{Cs}^+)}{r(\text{Cl}^-)} = \frac{0.170 \text{ nm}}{0.181 \text{ nm}} = 0.94 \) 
cubic coordination \( \text{CN} = 8 \)

for NaCl \( \frac{r(\text{Na}^+)}{r(\text{Cl}^-)} = \frac{0.102 \text{ nm}}{0.181 \text{ nm}} = 0.56 \) 
octahedral coordination \( \text{CN} = 6 \)
(c) cesium chloride crystal structure

- CsCl is ionically bonded with radius ratio = 0.94 and CN = 8
- 8 Cl\(^-\) ions surround a central Cs\(^+\) ion at the \((\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\) position
- CsBr, TlCl and TlBr have similar structure

**Example:** calculate the ionic packing factor for CsCl \((r(\text{Cs}^+) = 0.170 \text{ nm}, r(\text{Cl}^-) = 0.181 \text{ nm})\)

\[
\sqrt{3}a = 2r + 2R = 2(0.170 + 0.181) = 0.502 \text{ nm}
\]

\[
a = 0.405 \text{ nm}
\]

packing factor = \[
\frac{4/3\pi [(0.170)^3 + (0.181)^3]}{(0.405)^3}
\]

\[
= 0.68
\]
(d) sodium chloride crystal structure
  • highly ionically bonded with Na\(^+\) ions occupying octahedral sites between FCC Cl\(^-\) ions and radius ratio = 0.56, CN = 6
  • MgO, CaO, NiO and FeO have similar structures

\[
\begin{align*}
\text{ex. calculate the density of NaCl from the crystal structure} & \quad (r(\text{Na}^+) = 0.102 \text{ nm, } r(\text{Cl}^-) = 0.181 \text{ nm}) \\
4 \text{ Na}^+ \text{ and } 4 \text{ Cl}^- \text{ ions per unit cell} & \\
\text{mass of a NaCl unit cell} & = 4 \times (22.99 + 35.45) \times 1.67 \times 10^{-24} \\
& = 3.88 \times 10^{-22} \text{ g}
\end{align*}
\]
lattice constant $a = 2(R + r)$

$= 2(0.102 + 0.181) = 0.566$ nm

volume of unit cell $= a^3$

$= (0.566 \times 10^{-7}$ cm$)^3 = 1.81 \times 10^{-22}$ cm$^3$

density $= 3.88 \times 10^{-22}$ g/1.81 $\times 10^{-22}$ cm

$= 2.16$ g/cm$^3$

ex. calculate the linear density of Ca$^{2+}$ and O$^{2-}$ ions/nm in the [110] direction of CaO

$(r(Ca^{2+}) = 0.106$ nm, $r(O^{2-}) = 0.132$ nm)

$a = 2(R + r) = 2(0.106 + 0.132)$

$= 0.476$ nm

in [110] direction

$\rho_L = 2$ O$^{2-}$ ions/ $\sqrt{2a}$

$= 2$ O$^{2-}$ ions/ $\sqrt{2}(0.476$ nm$)$

$= 2.97$ O$^{2-}$ ions/nm (2.97 Ca$^{2+}$ ions/nm)

ex. calculate the planar density of Ca$^{2+}$ and O$^{2-}$ in ions/nm$^2$ on (111) plane

(111) plane contains 2 O$^{2-}$ (or 2 Ca$^{2+}$) ions

$A = \frac{1}{2} \left(\sqrt{2}a\right)\left(\frac{\sqrt{3}}{\sqrt{2}} a\right)$

$= \sqrt{3} a^2/2 = 0.196$ nm$^2$

$\rho_{planar} = 2$ O$^{2-}$ ions/ 0.196 nm$^2 = 10.2$ O$^{2-}$ ions/nm$^2$
(e) interstitial sites in FCC and HCP crystal lattices

- **octahedral interstitial sites** – 6 nearest atoms or ions equidistant from central void
- **tetrahedral interstitial sites** – 4 nearest atoms or ions equidistant from central void

- there are 4 octahedral sites and 8 tetrahedral sites per unit cell of FCC
• location of interstitial sites
  octahedral sites  tetrahedral sites

• there is also the same number of octahedral interstitial sites as atoms in HCP unit cell and twice as many tetrahedral sites as atoms

(f) zinc blende (ZnS) crystal structure
• 4 zinc and 4 sulfur atoms
• one type (Zn or S) occupies lattice points and another occupies interstitial sites of FCC unit cell.
• S atoms  \( (0,0,0) \quad (\frac{1}{2},\frac{1}{2},0) \)
  \( (\frac{1}{2},0,\frac{1}{2}) \quad (0,\frac{1}{2},\frac{1}{2}) \)
• Zn atoms  \( (\frac{3}{4},\frac{1}{4},\frac{1}{4}) \quad (\frac{1}{4},\frac{1}{4},\frac{3}{4}) \)
  \( (\frac{1}{4},\frac{3}{4},\frac{1}{4}) \quad (\frac{3}{4},\frac{3}{4},\frac{3}{4}) \)
- tetrahedrally covalently bonded (87% covalent character) with $CN = 8$
- CdS, InAs, InSb and ZnSe have similar structures

ex. calculate the density of zinc blende

$(r(Zn^{2+}) = 0.060 \text{ nm, } r(S^{2-}) = 0.174 \text{ nm})$

4 $Zn^{2+}$ and 4 $S^{2-}$ ions per unit cell

mass of unit cell $= 4 (65.37 + 32.06) \times 1.67 \times 10^{-24}$

$= 6.47 \times 10^{-22} \text{ g}$

lattice constant $\sqrt{3} a/4 = (R + r)$

$a = 4 (R + r)/ \sqrt{3} = 4(0.06 + 0.174)/\sqrt{3} = 0.540 \text{ nm}$

volume of unit cell $= (5.40 \times 10^{-8} \text{ cm})^3$

$= 1.57 \times 10^{-22} \text{ cm}^3$

density $= 6.47 \times 10^{-22} \text{ g}/1.57 \times 10^{-22} \text{ cm}^3 = 4.12 \text{ g/cm}^3$
(g) calcium fluoride (CaF$_2$) crystal structure
- Ca$^{2+}$ ions occupy the FCC lattice sites while F$^-$ ions are located at 8 tetrahedral sites
- UO$_2$, BaF$_2$, PbMg$_2$ have similar structures
- Large number of unoccupied octahedral sites in UO$_2$ allow it to be used as nuclear fuel
- Fission products are accommodated in these vacant positions

Ex. calculate the density of UO$_2$

\[ r(U^{4+}) = 0.105 \text{ nm, } r(O^{2-}) = 0.132 \text{ nm} \]

4 U$^{4+}$ and 8 O$^{2-}$ ions per unit cell

Mass of the unit cell = \((4 \times 238 + 8 \times 16) \times 1.67 \times 10^{-24} \)
= \(1.794 \times 10^{-21} \text{ g} \)

Lattice constant \( \sqrt{3}a = 2 (2R + 2r) \)
\[ a = 4(R + r)/\sqrt{3} = 4(0.105 + 0.132)/\sqrt{3} = 0.5474 \text{ nm} \]

Density = \(1.794 \times 10^{-21}/(5.474 \times 10^{-8})^3 = 10.9 \text{ g/cm}^3 \)
(h) antifluoride
- anions occupy lattice points and cations occupy eight tetrahedral sites of FCC
- examples – Li₂O, Na₂O, K₂O, Mg₂Si

(i) corundum (Al₂O₃) crystal structure
- oxygen ions in lattice points of HCP unit cell, 2 Al³⁺ ions in 2/3 octahedral sites for every 3 O²⁻ ions
- it leads to some distortion of structure

(j) spinel (MgAl₂O₄) crystal structure
- O²⁻ ions form FCC lattice and Mg²⁺ and Al³⁺ ions occupy interstitial sites
- these are nonmetallic magnetic materials

![Diagram of octahedral sites 2/3 occupied by Al³⁺ in spinel structure](image-url)
(k) perovskite (CaTiO$_3$) crystal structure
- Ca$^{2+}$ and O$^{2-}$ ions form FCC unit cell
  Ca$^{2+}$ ions occupy corners and O$^{2-}$ ions occupy face centers
  Ti$^{4+}$ ions are at octahedral sites
- other examples: BaTiO$_3$, SrTiO$_3$, CaZrO$_3$, SrZrO$_3$, LaAlO$_3$
(l) carbon and its allotropes

(i) graphite
• layered structure with carbon atoms in hexagonal arrays
• layers are bonded together by weak secondary bonds
• free electrons can easily travel from one side to the other in the same layer
• good lubricating properties

(ii) diamond
• the stiffest, hardest and least compressible material made by nature
• synthetic diamonds are used as cutting tools, coating, and abrasives
(iii) buckminster fullerenes (buckyball) $C_{60}$
- made of 12 pentagons and 20 hexagons
- diameter of the $C_{60}$ is 0.710 nm nanocluster
- aggregate form of $C_{60}$ has an FCC structure

(iv) carbon nanotubes
- the most frequently encountered diameter is 1.4 nm, length can be in μm or even mm
- single-wall nanotube (SWNT) and multiwall nanotube (MWNT) can be synthesized
- low density, high heat conductivity, high electron conductivity
(3) silicate structures
basic structure
• silicate ($\text{SiO}_4^{4-}$) tetrahedron is building block
• $\text{Si}—\text{O}$ bond: 50% ionic and 50% covalent
• $\text{SiO}_4^{4-}$ tetrahedrons are normally joined corner to corner and rarely edge to edge
• many different types of silicate structures can be produced
(a) island structure
  • positive ions bond with the oxygen of $\text{SiO}_4^{4-}$ tetrahedron such as $(\text{Mg, Fe})\text{SiO}_4$
(b) chain/ring structure
  • two corners of each $\text{SiO}_4^{4-}$ tetrahedron bonds with corners of other tetrahedron
  • chain $(\text{MgSiO}_3)$ or ring $(\text{Be}_3\text{Al}_2(\text{SiO}_3)_6)$ structure with the unit formula of $\text{SiO}_3^{2-}$ results
(c) **sheet structure**

- three corners of same planes of silicate tetrahedron bonded to the corners of three other silicate tetrahedra
- the unit chemical formula – $\text{Si}_2\text{O}_5^{2-}$

- each tetrahedron has one unbounded oxygen and hence chains can bond with other type of sheets
  if the bondings are weak, sheets slide over each other easily
(d) silicate networks

- **silica** – SiO$_2$ network in which all four corners of the SiO$_4$$^{4-}$ tetrahedra share oxygen atoms

- three basic structures – quartz, tridymite and cristobalite, the most stable forms of silica depend on the temperature range:
  - $< 573^\circ C$ low quartz
  - $573 \sim 867^\circ C$ high quartz
  - $867 \sim 1470^\circ C$ high tridymite
  - $> 1710^\circ C$ liquid

- **feldspars** – infinite 3D networks, some Al$^{3+}$ ions replace Si$^{4+}$ ions, net negative charge is balanced by alkaline and alkaline ions (Na$^+$, K$^+$, Ca$^{2+}$, Ba$^{2+}$) fit into interstitial sites
<table>
<thead>
<tr>
<th>Table 11.3</th>
<th>Ideal silicate mineral compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Silica:</strong></td>
<td>Common crystalline phases of SiO₂</td>
</tr>
<tr>
<td>Quartz</td>
<td>Al₂O₃ · 2SiO₂ · 2H₂O</td>
</tr>
<tr>
<td>Tridymite</td>
<td>Al₂O₃ · 4SiO₂ · H₂O</td>
</tr>
<tr>
<td>Cristobalite</td>
<td>Al₂O₃ · 2SiO₂</td>
</tr>
<tr>
<td><strong>Alumina silicate:</strong></td>
<td>Al₂O₃ · SiO₂</td>
</tr>
<tr>
<td>Kaolinite (china clay)</td>
<td>3Al₂O₃ · 2SiO₂</td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td>Al₂O₃ · 2SiO₂</td>
</tr>
<tr>
<td>Metakaolinite</td>
<td>Al₂O₃ · SiO₂</td>
</tr>
<tr>
<td>Sillimanite</td>
<td>3Al₂O₃ · 2SiO₂</td>
</tr>
<tr>
<td>Mullite</td>
<td></td>
</tr>
<tr>
<td><strong>Alkali alumina silicate:</strong></td>
<td></td>
</tr>
<tr>
<td>Potash feldspar</td>
<td>K₂O · Al₂O₃ · 6SiO₂</td>
</tr>
<tr>
<td>Soda feldspar</td>
<td>Na₂O · Al₂O₃ · 6SiO₂</td>
</tr>
<tr>
<td>(Muscovite) mica</td>
<td>K₂O · 3Al₂O₃ · 6SiO₂ · 2H₂O</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>Na₂O · 2MgO · 5Al₂O₃ · 24SiO₂ · (6 + n)H₂O</td>
</tr>
<tr>
<td>Leucite</td>
<td>K₂O · Al₂O₃ · 4SiO₂</td>
</tr>
<tr>
<td><strong>Magnesium silicate:</strong></td>
<td></td>
</tr>
<tr>
<td>Cordierite</td>
<td>2MgO · 5SiO₂ · 2Al₂O₃</td>
</tr>
<tr>
<td>Steatite</td>
<td>3MgO · 4SiO₂</td>
</tr>
<tr>
<td>Talc</td>
<td>3MgO · 4SiO₂ · H₂O</td>
</tr>
<tr>
<td>Chrysotile (asbestos)</td>
<td>3MgO · 2SiO₂ · 2H₂O</td>
</tr>
<tr>
<td>Forsterite</td>
<td>2MgO · SiO₂</td>
</tr>
</tbody>
</table>
(4) processing of ceramics produced by compacting powder or particles into shapes and heated to bond particles together
three basic steps:
(a) material preparation
particles and other ingredients (binders and lubricants) are ground and blend wet or dry
ex. spray-dried pellets of alumina ceramic

(b) forming or casting
• agglomerating particles formed in dry, plastic or liquid conditions
• cold forming process is predominant
• pressing, slip casting and extrusion are the common forming processes
(i) dry pressing – simultaneous uniaxial compaction and shaping of power along with binder in a die
wide variety of shapes can be formed rapidly and accurately
(ii) **isolatic pressing** – ceramic powder is loaded into a flexible, airtight container (bag) and pressure is applied outside the chamber with hydraulic fluid. The force of applied pressure is uniform in all directions. Examples: spark plug insulators, carbide tools, crucibles, bearings.

(iii) **hot pressing** – combing the pressing and firing operations. Both uniaxial and isostatic method are used.
(iv) **slip casting** – process that can cast ceramic shapes

- powdered ceramic material and a liquid mixed to prepare a stable suspension (called *slip*)
- slip is poured into porous mold and liquid portion is partially absorbed by mold layer of semi-hard material is formed against mold surface
- excess slip is poured out of cavity or cast as solid
- the material in mold is allowed to dry and then fired

![Diagram of slip casting](image-url)
(v) **extrusion** – single cross sections and hollow shapes of ceramics can be produced by extrusion

- plastic ceramic material is forced through a hard steel or alloy die by a motor driven augur

(c) thermal treatments

**drying** – parts are dried before firing to remove water from ceramic body,
- usually carried out at or below 100°C
- organic binder can be removed by heating in the range of 200~300°C

**sintering** – small particles are bonded together by solid state diffusion to produce dense, coherent product
- carried out at higher temperature but below melting point
• as process proceeds, larger particles are formed at the expense of the smaller ones

MgO sintered at 1430°C

(a) 30 min (f.p. = 0.39)  (b) 303 min (f.p. = 0.14)
(c) 1110 min (f.p. = 0.09)  (d) end of process

• the particles getting larger, the porosity of compacts decreases
• the driving force for the process is the lowering of the surface energy of the system

vitrification – during firing, glass phase liquefies and fills the pores upon cooling liquid phase of glass solidifies and a glass matrix that bonds the particles is formed
(5) traditional and engineering ceramics
(a) traditional ceramics
made up of clay, silica and feldspar
- **clay**: mainly hydrated aluminum silicates \(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}\) with small amount of other oxides
  provide workability and hardness

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>(\text{Al}_2\text{O}_3)</th>
<th>(\text{SiO}_2)</th>
<th>(\text{Fe}_2\text{O}_3)</th>
<th>(\text{Ti}_2\text{O}_3)</th>
<th>(\text{CaO})</th>
<th>(\text{MgO})</th>
<th>(\text{Na}_2\text{O})</th>
<th>(\text{K}_2\text{O})</th>
<th>(\text{H}_2\text{O})</th>
<th>Ignition loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>37.4</td>
<td>45.5</td>
<td>1.68</td>
<td>1.30</td>
<td>0.004</td>
<td>0.03</td>
<td>0.011</td>
<td>0.005</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>Tenn ball clay</td>
<td>30.9</td>
<td>54.0</td>
<td>0.74</td>
<td>1.50</td>
<td>0.14</td>
<td>0.20</td>
<td>0.45</td>
<td>0.72</td>
<td>...</td>
<td>11.4</td>
</tr>
<tr>
<td>Ky. ball clay</td>
<td>32.0</td>
<td>51.7</td>
<td>0.90</td>
<td>1.52</td>
<td>0.21</td>
<td>0.19</td>
<td>0.38</td>
<td>0.89</td>
<td>...</td>
<td>12.3</td>
</tr>
</tbody>
</table>

- **silica**: provide better temperature resistance and high melting point refractory component of traditional ceramic
- **potash feldspar**: the basic composition of \(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2\)
  makes a glass when ceramic is fired triaxial whiteware

<table>
<thead>
<tr>
<th>Type of clay</th>
<th>China clay</th>
<th>Ball clay</th>
<th>Feldspar</th>
<th>Flint</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard porcelain</td>
<td>40</td>
<td>10</td>
<td>25</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>Electrical insulation ware</td>
<td>27</td>
<td>14</td>
<td>26</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>Vitreous sanitary ware</td>
<td>30</td>
<td>20</td>
<td>34</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Electrical insulation</td>
<td>23</td>
<td>25</td>
<td>34</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Vitreous tile</td>
<td>26</td>
<td>30</td>
<td>32</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Semivitreous whiteware</td>
<td>23</td>
<td>30</td>
<td>25</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>Bone china</td>
<td>25</td>
<td>...</td>
<td>15</td>
<td>22</td>
<td>38 bone ash</td>
</tr>
<tr>
<td>Hotel china</td>
<td>31</td>
<td>10</td>
<td>22</td>
<td>35</td>
<td>2 CaCO_3</td>
</tr>
<tr>
<td>Dental porcelain</td>
<td>5</td>
<td>...</td>
<td>95</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
silica-leucite-mullite ternary phase diagram

what probably occurs during the firing of whiteware body

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Reactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 100</td>
<td>Loss of moisture</td>
</tr>
<tr>
<td>100–200</td>
<td>Removal of absorbed water</td>
</tr>
<tr>
<td>450</td>
<td>Dehydroxylation</td>
</tr>
<tr>
<td>500</td>
<td>Oxidation of organic matter</td>
</tr>
<tr>
<td>573</td>
<td>Quartz inversion to high form. Little overall volume damage</td>
</tr>
<tr>
<td>980</td>
<td>Spinel forms from clay. Start of shrinkage</td>
</tr>
<tr>
<td>1000</td>
<td>Primary mullite forms</td>
</tr>
<tr>
<td>1050–1100</td>
<td>Glass forms from feldspar, mullite grows, shrinkage continues</td>
</tr>
<tr>
<td>1200</td>
<td>More glass, mullite grows, pores closing, some quartz solution</td>
</tr>
<tr>
<td>1250</td>
<td>60% glass, 21% mullite, 19% quartz, pores at minimum</td>
</tr>
</tbody>
</table>
(b) engineering ceramics
pure or nearly pure compounds of chiefly oxides, carbides, nitrides

<table>
<thead>
<tr>
<th>Material</th>
<th>Density (g/cm³)</th>
<th>Compressive strength MPa ksi</th>
<th>Tensile strength MPa ksi</th>
<th>Flexural strength MPa ksi</th>
<th>Fracture toughness MPa√m ksi√m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃ (99%)</td>
<td>3.85</td>
<td>2585 375</td>
<td>207 30</td>
<td>345 50</td>
<td>4 3.63</td>
</tr>
<tr>
<td>Si₃N₄ (hot-pressed)</td>
<td>3.19</td>
<td>3450 500</td>
<td></td>
<td>690 100</td>
<td>6.6 5.99</td>
</tr>
<tr>
<td>Si₃N₄ (reaction-bonded)</td>
<td>2.8</td>
<td>770 112</td>
<td></td>
<td>255 37</td>
<td>3.6 3.27</td>
</tr>
<tr>
<td>SiC (sintered)</td>
<td>3.1</td>
<td>3860 560</td>
<td>170 25</td>
<td>550 80</td>
<td>4 3.63</td>
</tr>
<tr>
<td>ZrO₂, 9% MgO (partially stabilized)</td>
<td>5.5</td>
<td>1860 270</td>
<td></td>
<td>690 100</td>
<td>8+ 7.26+</td>
</tr>
</tbody>
</table>

**alumina (Al₂O₃)**
- used for refractory tubing, high-purity crucibles and park plug insulator material
- commonly doped with MgO, cold pressed and sintered to form uniform grain structure
- used for electric application

**silicon nitride (Si₃N₄)**
- has the most useful combination of engineering properties
- compact of Si powder is nitrided in a flow of nitrogen gas to produce microporous Si₃N₄ with moderate strength
- used for parts of advanced engines
silicon carbide (SiC):
• hard, refractory carbide with outstanding resistance to oxidation at high temperature
• can be sintered at 2100°C
• commonly used as reinforcement in composite materials

zirconia (ZrO₂)
• polymorphic and transforms from tetragonal to monoclinic structure at 1170°C and is subject to cracking
• combined with 9% MgO can produce a partially stabilized zirconia (PSZ) ceramic with high fracture toughness
(6) mechanical properties of ceramics
strength of ceramics vary greatly but they are generally **brittle**
compressive strength is (5 to 10 times) higher than tensile strength
(a) mechanism of deformation
• covalently bonded ceramics: exhibit brittle fracture due to separation of electron-pair bonds without their subsequent reformation
• ionically bonded ceramics: single crystal show considerable plastic deformation
• polycrystalline ceramics are brittle
  ex. NaCl crystal
  slip of planes is rarely observed as same charges come into contact
  cracking occurs at grain boundaries
(b) factors affecting strength

• failure occurs mainly from **surface defects**
• **pores** gives rise to stress concentration and cracks
• pores reduce effective cross-sectional area

• flaw size is related to **grain size**
• finer size ceramics have smaller flaws and hence are stronger.
• composition, microstructure, surface condition, temperature and environment also determine strength

![Graph showing the relationship between volume fraction of pores and transverse strength](image-url)
(c) toughness of ceramic materials
• ceramics have low strength
• research has been conducted to improve toughness
• **hot pressing with additives** and reaction bonding improve toughness
• $K_{IC}$ values obtained by *four point bend test*

\[ K_{IC} = Y \sigma_f \sqrt{\pi a} \]

$\sigma_f$ : fracture stress (MPa)
$a$ : half size of target internal flaw
$Y$ : dimensionless constant

ex. a silicon nitride ceramic has a strength of 300 MPa and a fracture toughness of 3.6 MPa$\sqrt{\text{m}}$, what is the large-size internal crack that the material can support without fracturing? ($Y = 1$)

\[ K_{IC} = Y \sigma_f \sqrt{\pi a} = 3.6 \text{ MPa} \sqrt{\text{m}} \]

\[
\begin{align*}
a &= \frac{K_{IC}^2}{\pi Y^2 \sigma_f^2} \\
&= \frac{(3.6 \text{ MPa} \sqrt{\text{m}})^2}{\pi (1)^2 (300 \text{ Mpa})^2} \\
&= 4.58 \times 10^{-5} \text{ m} \\
&= 45.8 \mu \text{m}
\end{align*}
\]

the largest internal crack = $2a = 91.6 \mu \text{m}$
(d) transformation toughening of partially stabilized ZrO$_2$ (PSZ)

- transformation of zirconia combined with some other refractory oxides (MgO) can produce very high toughness ceramics.
- ZrO$_2$ exists in 3 structures
  - monoclinic up to 1170$^\circ$C
  - tetragonal 1170 – 2370$^\circ$C
  - cubic above 2370$^\circ$C
- if a mixture of ZrO$_2$-9 mol% MgO is sintered at about 1800$^\circ$C and rapidly cooled, it will be in metastable cubic structure
• if reheated to 1400°C and held for sufficient time tetragonal structure precipitates
• under action of stress, this tetragonal structure transforms to monoclinic increasing volume and hence retarding crack growth

(e) fatigue failure
• fatigue fracture in ceramics is rare due to absence of plastic deformation
• straight fatigue crack in has been reported in alumina after 79,000 compression cycles
• ceramics are hard and can be used as abrasives
(7) thermal properties of ceramics
- most ceramics have low thermal conductivities and are good thermal insulators
- due to high heat resistance, many ceramics are used as industrial refractories
- \( \text{Al}_2\text{O}_3 \) and \( \text{MgO} \) are expensive and difficult to form into shapes, thus not used as refractories
- most industrial refractories are made of mixture of ceramic compounds

![Image]

**Table 11.8** Compositions and applications for some refractory brick materials

<table>
<thead>
<tr>
<th>Composition (wt %)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidic types:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silica brick</td>
<td>95–99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Superduty fireclay brick</td>
<td>53</td>
<td>42</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-duty fireclay brick</td>
<td>51–54</td>
<td>37–41</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High-alumina brick</td>
<td>0–50</td>
<td>45–99+</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Basic types:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Magnesite</td>
<td>0.5–5</td>
<td>91–98</td>
<td>18–24 Cr₂O₃</td>
<td>0.6–4 CaO</td>
</tr>
<tr>
<td>Magnesite-chrome</td>
<td>2–7</td>
<td>50–82</td>
<td>38–50</td>
<td>38–58 CaO</td>
</tr>
<tr>
<td>Dolomite (burned)</td>
<td>6–13</td>
<td>38–50</td>
<td>38–58 CaO</td>
<td></td>
</tr>
<tr>
<td>Special types:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zircon</td>
<td>32</td>
<td>66 ZrO₂</td>
<td>91 SiC</td>
<td></td>
</tr>
<tr>
<td>Silicon carbide</td>
<td>6</td>
<td>2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Applications for some refractories:
- **Superduty fireclay bricks**: linings for aluminum-melting furnaces, rotary kilns, blast furnaces, and hot-metal transfer ladles
- **High-duty fireclay brick**: linings for cement and lime kilns, blast furnaces, and incinerators
- **High-alumina brick**: boiler furnaces, spent-acid regenerating furnaces, phosphate furnaces, glass-tank refiner walls, carbon black furnaces, continuous-casting tundish linings, coal gasification reactor linings, and petroleum coke kilns
- **Silica brick**: chemical reactor linings, glass tank parts, ceramic kilns, and coke ovens
- **Magnesite brick**: basic-oxygen-process furnace linings for steelmaking
- **Zircon brick**: glass-tank bottom paving and continuous-casting nozzles

- important properties of ceramic refractory materials: (i) low- and high-temperature strengths, (ii) bulk density, and (iii) porosity
- dense refractories with low porosity have high resistance to corrosion and erosion
- a high amount of porosity is desirable for insulating refractories
(a) acidic refractories
- silica refractories have high refractoriness, high mechanical strength and rigidity
- fireclays – mixture of plastic fireclay, flint clay and clay grog
- high-aluminum refractories contain 50-90% alumina and have higher fusion temperature

(b) basic refractories
- consists mainly of MgO, CaO, chrome ore
- have bulk densities, high melting points and good resistance to chemical attack

(c) insulation for space shuttle orbiter
- about 70% of external surface is protected from heat by 24000 ceramic tiles made from a silica-fiber compound
- high-temperature reusable-surface insulation (HRSI) – density is 4 kg/ft^3 and can withstands temperatures as high as 1260°C
(8) glasses
- inorganic products of fusion that has cooled to a rigid condition without crystallization
- glass has amorphous structure
- combination of transparency, hardness, sufficient strength, and corrosion resistance

(a) glass transition temperature $T_g$
- glass does not crystallize upon cooling, it transforms from rubbery material to rigid, brittle glassy state in a narrow temperature range
(b) structure of glasses

- based on **glass-forming oxide** silica $\text{SiO}_2$
  - fundamental subunit of glass is $\text{SiO}_4^{4-}$ tetrahedron – $\text{Si}^{4+}$ ion is covalently ionically bonded to four oxygen atoms
- in cristobalite, Si-O tetrahedron are joined corner to corner to form long range order
- in simple silica glass, tetrahedra are joined corner to corner to form loose network

- **glass modifying oxides**
  - network modifiers – oxides that breakup the glass network, added to glass to increase workability ex. $\text{Na}_2\text{O}$, $\text{K}_2\text{O}$, $\text{CaO}$, $\text{MgO}$
  - oxygen atoms enter network other ions stay in interstices, by filling some interstices, these ions promote crystallization of glass
• **intermediate oxides** – cannot form glass network by themselves but can join into an existing network ex. Al$_2$O$_3$, lead oxide added to silica glass to obtain special properties

(c) **composition of glasses**

- **soda lime glass** – the most common glass (90%) composition: 71-73% SiO$_2$, 12-14% Na$_2$O, 10-12% CaO easier to form and used in flat glass and containers
- **borosilicate glass** – replacement of alkali oxides by boric oxide in silica glass network.
known as **Pyrex glass** and is used for lab equipments and piping.  
• **lead glass** – lead oxide acts as network modifier and network former  
  low melting point – used for solder sealing.  
  used in radiation shields, optical glass and TV bulbs.

<table>
<thead>
<tr>
<th>Glass</th>
<th>SiO₂</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CaO</th>
<th>B₂O₃</th>
<th>Al₂O₃</th>
<th>Other</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. (Fused) silica</td>
<td>99.5+</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Difficult to melt and fabricate but usable to 1000°C. Very low expansion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>and high thermal shock resistance. Fabricate from relatively soft borosilicate glass; heat to separate SiO₂ and B₂O₃ phases; acid leach B₂O₃ phase; heat to consolidate pores.</td>
</tr>
<tr>
<td>2. 96% silica</td>
<td>96.3</td>
<td>&lt;0.2</td>
<td>&lt;0.2</td>
<td>2.9</td>
<td>0.4</td>
<td></td>
<td></td>
<td>Easily fabricated. Widely used in slightly varying grades, for windows, containers, and electric bulbs.</td>
</tr>
<tr>
<td>3. Soda-lime: plate glass</td>
<td>71–73</td>
<td>12–14</td>
<td>10–12</td>
<td>0.5–1.5</td>
<td>MgO, 1–4</td>
<td></td>
<td></td>
<td>Readily melted and fabricated with good electrical properties. High lead absorbs x-rays; high refractive used in achromatic lenses. Decorative crystal glass. Low expansion, good thermal shock resistance, and chemical stability. Widely used in chemical industry.</td>
</tr>
<tr>
<td>4. Lead silicate: electrical</td>
<td>63</td>
<td>7.6</td>
<td>6</td>
<td>0.3</td>
<td>0.6</td>
<td>PbO, 21</td>
<td>MgO, 0.2</td>
<td>Low dielectric loss. Increased alumina, lower boric oxide improves chemical durability. Widely used for fibers in glass resin composites. High-temperature strength, low expansion.</td>
</tr>
<tr>
<td>5. High-lead</td>
<td>35</td>
<td>7.2</td>
<td></td>
<td></td>
<td></td>
<td>PbO, 58</td>
<td></td>
<td>Crystalline ceramic made by devitrifying glass. Easy fabrication (as glass), good properties. Various glasses and catalysts.</td>
</tr>
<tr>
<td>6. Borosilicate: low expansion</td>
<td>80.5</td>
<td>3.8</td>
<td>0.4</td>
<td></td>
<td>12.9</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7. Low electrical loss</td>
<td>70.0</td>
<td>6.4</td>
<td>0.5</td>
<td>28.0</td>
<td>1.1</td>
<td>PbO, 1.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Aluminoborosilicate: standard apparatus</td>
<td>74.7</td>
<td>6.4</td>
<td>0.5</td>
<td>9.6</td>
<td>5.6</td>
<td>B₂O₃, 2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Low alkali (E-glass)</td>
<td>54.5</td>
<td>0.5</td>
<td>22</td>
<td>8.5</td>
<td>14.5</td>
<td>MgO, 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10. Aluminosilicate</td>
<td>57</td>
<td>1.0</td>
<td>5.5</td>
<td>4</td>
<td>20.5</td>
<td>MgO, 12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11. Glass-ceramic</td>
<td>40–70</td>
<td>10–35</td>
<td>MgO, 10–30</td>
<td>TiO₂, 7–15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(d) Viscous deformation of glasses behave as a viscous liquid above $T_g$ and viscosity decreases with increase in temperature

$$\eta = \eta_0 e^{Q/RT}$$

$Q$: molar activation energy for viscous flow
$\eta$: viscosity of glass (Pa·s)
$\eta_0$: preexponential constant (Pa·s)
$R$: gas constant
(i) **working point** \( (\eta = 10^3 \text{ Pa}\cdot\text{s}) \) – glass fabrication can be carried out
(ii) **softening point** \( (\eta = 10^7 \text{ Pa}\cdot\text{s}) \) – glass flows under its own weight
(iii) **annealing point** \( (\eta = 10^{12} \text{ Pa}\cdot\text{s}) \) – internal stresses can be relieved
(iv) **strain point** \( (\eta = 10^{13.5} \text{ Pa}\cdot\text{s}) \) – glass is rigid below this point

• interval between the annealing and strain points is commonly considered the annealing range of a glass

ex. a 96% silica glass has a viscosity of \( 10^{13} \text{ P} \) at its annealing point of 940°C and a viscosity of \( 10^8 \text{ P} \) at its softening point of 1470°C, calculate the activation energy in kJ/mol for the viscous flow of this glass

\[
\frac{\eta_{ap}}{\eta_{sp}} = \exp \left[ \frac{Q}{8.314} \left( \frac{1}{1213} - \frac{1}{1743} \right) \right] = \frac{10^{13}}{10^8} = 10^5
\]

\[
\ln 10^5 = \frac{Q}{8.314} (8.244 \times 10^{-4} - 5.737 \times 10^{-4})
\]

\[
11.5 = Q (3.01 \times 10^{-5})
\]

\[
Q = 3.82 \times 10^5 \text{ J/mol} = 382 \text{ kJ/mol}
\]
(e) forming methods for glass
  • float-glass process – forming sheet and plate glass

  ![Diagram of float-glass process]

  • blowing, pressing and casting of glass

  ![Diagram of blowing and casting]

(f) tempered glass
  • glass is heated into near softening point and rapidly cooled
  • surface cools first and contracts causing tensile stresses in the interior and compressive stress on the surface
  • tempering treatment increases strength of the glass
(g) chemically strengthened glass special treatment increases chemical resistance of glasses
ex. sodium aluminosilicate glasses are immersed in a bath of KNO$_3$ at 50$^\circ$C for 6~10 hours
• large K$^+$ ions are induced into surface causing compressive stress
• compressive layer is much thinner than that in thermal tempering
• used for supersonic aircraft glazing and ophthalmic lenses
(9) ceramics in biomedical applications
- orthopedic implant

- eyeglass
- laboratory ware
- thermometers
- dental applications