TOPIC 6. CERAMIC MATERIALS

• Introduction
• Structure of Ceramic Materials
• Glasses
  • Mechanical Properties of Ceramic Materials
  • Processing of Ceramic Materials
  • Examples of applications
INTRODUCTION

*Inorganic Materials made from Metals and Non Metals united by ionic and/or covalent bonds*

Can be: crystalline, amorphous or mixture of both

**GENERAL PROPERTIES**

- Hardness
- Britteness
- Electrical conductivity $\sigma_{\text{electric}}$
- Thermal conductivity $\sigma_{\text{thermal}}$
- Compression strength $R_{\text{compression}}$
- Melting point $T_m$
- Chemical Stability
### GENERAL PROPERTIES

- **High Young’s Modulus and high melting points**
  - Strong bonds (covalent and/or ionic)

- **Limited electrical and thermal conductivity**
  - Absence of electronic cloud (directional bond)

- **Low thermal shock resistance**
  - Coefficients of thermal expansion and thermal conductivity are low

- **Refractory**
  - Stability at high temperature (NO CREEP)

- **Resistance to oxidation/corrosion**
  - Chemical stability
CLASSIFICATION

Glasses

Based on SiO$_2$ + additives for ↓ $T_f$

Traditional Ceramics (clay products)

- Porous ceramics (bricks, pottery, china)
- Compact ceramics (porcelain, earthware)
- Refractory ceramics

Clay: Al$_2$O$_3$·SiO$_2$·H$_2$O
Silica: SiO$_2$
Feldspar: K$_2$O·Al$_2$O$_3$·6SiO$_2$

Engineering Ceramics or Advanced Ceramics:

- Refractory ceramics (SiC, Al$_2$O$_3$, ZrO$_2$, BeO, MgO).
- Piezoelectrics and Ferroelectrics: BaTiO$_3$, SrTiO$_3$
- Electro-optics: LiNbO$_3$
- Abrasive ceramics: nitrides and carbides Si$_3$N$_4$, SiC
- Molecular membranes
- Superconductive ceramics (YBa$_2$Cu$_3$O$_7$)
- Biomaterials: Hydroxyapatite


**STRUCTURE**

**Ceramic Bonds**

Pauling: $\% \text{ Ionic character} = 100 \cdot \left[ 1 - e^{-\frac{(X_A - X_B)^2}{4}} \right]$  

Percentage of ionic and covalent character of the bond for some ceramic materials determines the CRystalline Structure

<table>
<thead>
<tr>
<th>Ceramic Material</th>
<th>Atoms in bond</th>
<th>$X_A - X_B$</th>
<th>% Ionic Character</th>
<th>% Covalent Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>Mg—O</td>
<td>2,3</td>
<td>73</td>
<td>27</td>
</tr>
<tr>
<td>$\text{Al}_2\text{O}_3$</td>
<td>Al—O</td>
<td>2,0</td>
<td>63</td>
<td>37</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>Si—O</td>
<td>1,7</td>
<td>51</td>
<td>49</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>Si—N</td>
<td>1,2</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>SiC</td>
<td>Si—C</td>
<td>0,7</td>
<td>11</td>
<td>89</td>
</tr>
</tbody>
</table>
STRUCTURE

T2 STRUCTURES:

- Ions packing
- Electroneutrality of ionic ceramics
- Crystalline type structures
**Ionic structure**: packing of anions with cations in interstitials

Sizes $C^+ A^- \Rightarrow r_{\text{cation}} < r_{\text{anion}}$

**Electroneutrality**

**Coordination Index** (By increasing C.I $\Rightarrow$ increase stability)

**Sharing of polyhedral** (sharing vertices instead of edges or faces (increases the distance between cations))
PACKING OF IONS

The relation between radius when A⁻ and C⁺ are in contact. ⇒ Relation of radius is critical (minimum)

<table>
<thead>
<tr>
<th>Arrangement of A⁻ around C⁺ central and C.I.</th>
<th>Cation/anion Radius ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C.I. 8 Corners of a cube</td>
<td>0.732-1.0</td>
</tr>
<tr>
<td>C.I. 6 Corners of an octahedron</td>
<td>0.414-0.732</td>
</tr>
<tr>
<td>C.I. 4 Corners of a tetrahedron</td>
<td>0.225-0.414</td>
</tr>
<tr>
<td>C.I. 3 Corners of a triangle</td>
<td>0.155-0.225</td>
</tr>
</tbody>
</table>
SIMPLE CUBIC STRUCTURE: CsCl

- $\text{Cl}^-$: cubic
- $\text{Cs}^+$: centre of the cube
- C.I.: 8

Ceramics that have this type of structure: **CsBr**, **TICl**, **TIBr**.

$$\frac{r_{\text{Cs}^+}}{r_{\text{Cl}^-}} = 0.94 > 0.732 \Rightarrow C.I. = 8 \Rightarrow \text{Cubic structure}$$
Ceramics that have this type of structure: MgO, CaO, FeO, NiO

- Cl\(^{-}\): FCC packing
- Na: all octahedral interstitials.
- 4 Na\(^{+}\) and 4 Cl\(^{-}\) per unit cell C.I.=6

\[ \frac{r_{Na^{+}}}{r_{Cl^{-}}} = 0.56 > 0.414 \Rightarrow C.I. = 6 \Rightarrow \text{Octahedral coord.} \]
FCC STRUCTURE: Zn Blende-ZnS

- $S^{2-}$: FCC packing
- $Zn^{2+}$: $\frac{1}{2}$ tetrahedral interstitials
- 4 $Zn^{2+}$ and 4 $S^{2-}$ per unit cell

According to Pauling bond $Zn-S \sim 87\%$ covalent

Ceramics that have this type of structure: Typical semiconductors: $CdS$, $HgTe$, $NiAs$, $SiC$, $GaAs$
HCP STRUCTURE: CORUNDUM (ALUMINA)

- $\text{O}^{2-}$: HCP packing $\rightarrow$ 6 ions
- $\text{Al}^{3+}$: 2/3 octahedral interstitials $\rightarrow$ 4 ions
- I.C.($\text{Al}^{3+}$): 6 ; I.C.($\text{O}^{2-}$): 6

Ceramics that have this type of structure: $\text{Cr}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, $\text{Al}_2\text{O}_3$...
CRYSITALLINE STRUCTURE OF PEROVSKITE ABO$_3$

A and B cations with different size ($r_A >> r_B$)

- O$^2-$ and Ca$^{2+}$: fcc packing
- Ti$^{4+}$: 1/4 octahedral sites
- C.I.(Ti$^{2+}$): 6; C.I.(Ca$^{2+}$): 12

Ceramics that adopt this type structure:
- BaTiO$_3$, CaTiO$_3$, SrTiO$_3$, PbZrO$_3$, KNbO$_3$, LiNbO$_3$, ...

Ferroelectric Materials,
Magnetic Superconductor properties
(YBa$_2$Cu$_3$O$_7$)
# Summary of Some Common Ceramic Crystal Structures

<table>
<thead>
<tr>
<th>Structure name</th>
<th>Structure type</th>
<th>Anion packing</th>
<th>Coordination numbers</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock salt (sodium chloride)</td>
<td>AX</td>
<td>FCC</td>
<td>cation: 6, anion: 6</td>
<td>NaCl, MgO, FeO</td>
</tr>
<tr>
<td>Cesium chloride</td>
<td>AX</td>
<td>Simple cubic</td>
<td>cation: 8, anion: 8</td>
<td>CsCl</td>
</tr>
<tr>
<td>Zinc Blende (sphalerite)</td>
<td>AX</td>
<td>FCC</td>
<td>cation: 4, anion: 4</td>
<td>ZnS, SiC</td>
</tr>
<tr>
<td>Fluorite</td>
<td>AX₂</td>
<td>Simple cubic</td>
<td>cation: 8, anion: 4</td>
<td>CaF₂, UO₂ThO₂</td>
</tr>
<tr>
<td>Perovskite</td>
<td>ABX₃</td>
<td>FCC</td>
<td>cation: 12 (A), 6 (B)</td>
<td>BaTiO₃, SrZrO₃, SrSnO₃</td>
</tr>
<tr>
<td>Spinel</td>
<td>AB₂X₄</td>
<td>FCC</td>
<td>cation: 4(A), 6(B),</td>
<td>MgAl₂O₄, FeAl₂O₄</td>
</tr>
</tbody>
</table>

Sophia A. Tsipas / Francisco Velasco / Belén Levenfeld
COVALENT CERAMICS
They are structural ceramics

**DIAMOND** → Structure type blend

C → sp³ → c.i. 4 → Tetrahedral CC₄. Bond 100% covalent.

- ↑ wear resistance
- ↑ hardness
- ↑ tensile strength
- Insulator

**SiC** → Diamond type structure (spherullite)

- Applications: Good abrasive properties. 89% covalent bond
- High hardness, chemically inert.
COVALENT CERAMICS
They are structural ceramics

**Si₃N₄ → Cutting Elements, blades, rotors**

Si → sp³ → c.i. 4 → SiN₄ Tetrahedra
N → sp² → c.i. 3 → N coordinated to 3 Si
Open structure.
70% covalent bond

**β-SiN₄**

Sialons **Si₆₋zAl₂O₂N₈₋z (1971)**

It is a solid solution between nitrides and oxides. Derived from Si₃N₄, by substituting z atoms of Si for Al atoms. In order to compensate the valence difference, the same number of N atoms are substituted by O. Cutting tools, antifriction rollers, motors components.
STRUCTURE OF SILICATES

Si and O are the most abundant elements in the earth’s crust
They are the base of traditional ceramics

Useful engineering materials because

- Low price
- Great availability
- Special properties

<table>
<thead>
<tr>
<th>Ceramic</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>K$_2$O</th>
<th>MgO</th>
<th>CaO</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica refractory</td>
<td>96</td>
<td></td>
<td></td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fireclay refractory</td>
<td>50-70</td>
<td>45-25</td>
<td></td>
<td>5</td>
<td></td>
<td></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>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steatite porcelain</td>
<td>64</td>
<td>5</td>
<td>30</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Portland cement</td>
<td>25</td>
<td>9</td>
<td></td>
<td>64</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Composition of some silicate ceramics

Fundamentally in:

- Construction (bricks, cement, glass)
- Electrical and thermal insulating materials
STRUCTURE OF SILICATES

- Si in tetrahedral coordination
- Bond type (Pauling): 50% ionic - 50% covalent
- $r_C/r_A = 0.29 \rightarrow$ stable structure with tetrahedral coordination.
- ↑ packing factor $\Rightarrow$ tetrahedra united in the corners.
- Multitude of possible structures:
  a) Structures of isolated silicates
  b) Ring and Chain structures
  c) Laminar structures
  d) 3D structures
## STRUCTURE OF SILICATES

Classification of silicates as a function of the tetrahedra ordering $[\text{SiO}_4]^{4-}$. 

<table>
<thead>
<tr>
<th>Type</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Orthosilicates or olivines</strong></td>
<td>(island tetrahedra $\text{SiO}_4^{4-}$)</td>
</tr>
<tr>
<td>Example: Forsterite ($\text{Mg}_2\text{SiO}_4$)</td>
<td></td>
</tr>
<tr>
<td><strong>pyrosilicate</strong></td>
<td>(island tetrahedra $\text{Si}_2\text{O}_7^{6-}$)</td>
</tr>
<tr>
<td>Example: ($\text{Ca}_2\text{MgSi}_2\text{O}_7$)</td>
<td></td>
</tr>
<tr>
<td><strong>metasilicates</strong></td>
<td>($\text{SiO}_3)_n^{2n-}$ (ring and chain structures)</td>
</tr>
<tr>
<td>Ring structures</td>
<td></td>
</tr>
<tr>
<td>Examples: Wollastonite ($\text{CaSiO}_3$), beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$</td>
<td></td>
</tr>
<tr>
<td>chain structures</td>
<td></td>
</tr>
<tr>
<td>Example: Enstatite ($\text{MgSiO}_3$)</td>
<td></td>
</tr>
<tr>
<td><strong>sheet or layered silicates</strong></td>
<td>($\text{Si}_2\text{O}_5)^{2-}$</td>
</tr>
<tr>
<td>Example: Kaolinite clay $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$</td>
<td>are talc $[\text{Mg}_3(\text{Si}_2\text{O}_5)_2(\text{OH})_2]$ micas [e.g., muscovite, $\text{KAl}_3\text{Si}<em>3\text{O}</em>{10}(\text{OH})_2$]</td>
</tr>
<tr>
<td><strong>3D</strong> ($\text{SiO}_2$)</td>
<td>Quartz, tridymite, cristobalite ($\text{SiO}_2$)</td>
</tr>
</tbody>
</table>
STRUCTURE OF SILICATES

Metasilicates (Ring and Chain Structure)

2 of the 4 O\(^-\) atoms in the tetrahedral SiO\(_4\)\(^4-\) are united to another tetrahedral in order to form \textbf{chains of silicate}.

\textbf{Formula: } (SiO\(_3\))\(_n\)\(^{2n-}\)

![Chain Structure](http://commons.wikimedia.org/wiki/File:Wollastonite_a_%2B_c.png)

![Ring Structure](http://commons.wikimedia.org/wiki/File:Cyclosilicates_3.svg)

Wollastonite (CaSiO\(_3\))
STRUCTURE OF SILICATES

Sheet or layered structure
3 of the 4 O\(^{-}\) atoms of in the tetrahedral SiO\(_4\)\(^{4-}\) are united to another tetrahedral in order to form layers of silicates

Formula: Si\(_2\)O\(_5\)\(^{2-}\)

- Kaolinite Al\(_2\)(OH)\(_4\)\(^{2+}\)
- Talc: Mg\(_3\)(OH)\(_4\)\(^{2+}\)

There is one O\(^{-}\) without bond in each tetrahedral
⇒ charge (-) ⇒ Joining laminas (+)

Formation of KAOLINITE

KAOLINITE

Si\(_2\)O\(_5\)\(^{2-}\)

Al\(_2\)(OH)\(_4\) Si\(_2\)O\(_5\)

Electrically neutral
## STRUCTURE OF SILICATES

### Three-Dimensional Silicates

<table>
<thead>
<tr>
<th>Silica</th>
<th>Feldspars</th>
</tr>
</thead>
<tbody>
<tr>
<td>- They share all the corners in the tetrahedra</td>
<td>- Similar structure to Silica ($\text{Al}^{3+}$ replaces $\text{Si}^{4+}$) ⇒ lattice with (-) charge ⇒ compensates the charge with voluminous cations ($\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$) in interstitial positions.</td>
</tr>
<tr>
<td>- Unit formula: $\text{SiO}_2$</td>
<td>- Principal component of traditional ceramics</td>
</tr>
<tr>
<td>- Presents Allotropy</td>
<td></td>
</tr>
<tr>
<td>- Important component in many traditional ceramics and many types of glasses</td>
<td></td>
</tr>
</tbody>
</table>

- **$\alpha$-quartz**
- **$\beta$-quartz**
- **$\beta$-cristobalite**
**NON CRYSTALLINE CERAMICS : GLASSES**

**Behaviour of glass during solidification**

**Crystalline Solid**
- As $\downarrow T$, crystallizes in $T_m$

**GLASS**
- As $\downarrow T$, $\uparrow$ viscosity
- Plastic stage $\Leftrightarrow$ Rigid stage

**Diagram**

- Supercooled liquid
- Glass
- Crystalline s.
- Contraction due to freezing

Volume (per unit mass) vs. Temp

$T_g$, $T_m$
CONSTITUENTS OF GLASSES

3 types of oxides

Glass Formers
SiO₂ and B₂O₃

Glass modifiers
(Na₂O, K₂O) and (CaO and MgO)

Intermediates: Al₂O₃
DO NOT form glasses only by themselves.

They are incorporated in the silicate lattice

- Al₂O₃ \( \rightarrow \) tetrahedra AlO₄⁻ replacing SiO₄⁻

- Charge defects (Al³⁺: Si⁴⁺) compensating with alkaline cations and alkaline earths.

Improve special properties:

- Al₂O₃ \( \rightarrow \) ↑ strength at high T (aluminosilicate glasses)

- PbO
  - Modifies optical properties
  - ↓ Tᵣ (glass soldering)
  - Radiation protection of ↑ E
CONSTITUENTS OF GLASSES

Substances constituents of glasses

<table>
<thead>
<tr>
<th>COLOURS THAT METALLIC IONS GIVE TO GLASSES</th>
</tr>
</thead>
<tbody>
<tr>
<td>ION</td>
</tr>
<tr>
<td>----------------</td>
</tr>
<tr>
<td>Cr³⁺</td>
</tr>
<tr>
<td>Cr⁶⁺</td>
</tr>
<tr>
<td>Cu²⁺</td>
</tr>
<tr>
<td>Cu⁺</td>
</tr>
<tr>
<td>Co²⁺</td>
</tr>
<tr>
<td>Ni²⁺</td>
</tr>
<tr>
<td>Mn²⁺</td>
</tr>
<tr>
<td>Mn³⁺</td>
</tr>
<tr>
<td>Fe²⁺</td>
</tr>
<tr>
<td>Fe³⁺</td>
</tr>
<tr>
<td>U⁶⁺</td>
</tr>
<tr>
<td>V³⁺</td>
</tr>
<tr>
<td>V⁴⁺</td>
</tr>
</tbody>
</table>
PROPERTIES OF GLASSES

Mechanical Properties

Brittle Materials ($E \uparrow \uparrow$ elastic modulus) = $f$ (composition, macroscopic (surface) imperfections, volume of material and $T$)
Low modulus of Weibull
Mechanical strength ↓ (presence of water/air + humidity)

Electrical Properties

Generally insulators ($\sigma \approx 10^{-10} - 10^{-20} \ \Omega\text{cm}^{-1}$)
$\sigma \uparrow \uparrow$ with Temperature
$\sigma \uparrow \uparrow$ with modifier ($=f$(size and amount of modifier))

Thermal Shock

$\uparrow \uparrow \alpha = \downarrow R_{\text{thermal shock}}$

| Material                                      | Thermal Expansion coeff. $({}^\circ\text{C}^{-1})$ | Thermal Shock failure $({}^\circ\text{C})$
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime glass</td>
<td>$10^{-5}$</td>
<td>80</td>
</tr>
<tr>
<td>Sodium borosilicate (Pyrex™ type)</td>
<td>$10^{-4}$</td>
<td>270</td>
</tr>
<tr>
<td>Fused silica</td>
<td>$10^{-6}$</td>
<td>1600</td>
</tr>
<tr>
<td>Lithia-alumina-silicate glass ceramic (Pyroceram™ type)</td>
<td>$10^{-6}$</td>
<td>670</td>
</tr>
<tr>
<td>Transparent lithia-alumina-silicate glass ceramic (Visions™ type)</td>
<td>$10^{-6}$</td>
<td>1330</td>
</tr>
</tbody>
</table>

Thermal shock resistance of common glasses and glass ceramics