Ch. 12

High Temperature Materials

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Ceramic materials are inorganic and non-metallic materials. Most of them are compounds between metallic and non-metallic elements for which the inter-atomic bonds are either totally ionic, or predominantly ionic but having some covalent character.

Ceramics used in electronic, computer, communication, aerospace and a host of other industries
Their crystal structures are generally more complex than those for metals.

The atomic boning (purely ionic – totally covalent)

Many ceramics

Combination of these bonding

% ionic character = \[ 1 - \exp(-0.25)(X_a - X_b)^2 \] \times 100

\( X_a \) and \( X_b \) are the electro-negativities for the respective elements from table 2.7 p. 19

<table>
<thead>
<tr>
<th>Substance</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>SiN4</td>
<td>30</td>
</tr>
<tr>
<td>ZnS</td>
<td>18</td>
</tr>
<tr>
<td>SiC</td>
<td>12</td>
</tr>
</tbody>
</table>

% Ionic character of inter-atomic Bonds
For Ceramic materials

Crystal structures

Metallic ions or cations

atomic bonding (ionic)

Electrically charged ions

+ charge (the valence electrons moved to non-metallic ions or anions (-charge)

The magnitude of the electrical charge on each component ions

The relative sizes of cations and anions

The crystal must be electrically neutral (total cations (+charge) = total anions (-charge) e.g., CaF$_2$ (Ca$^{+2}, 2F^{-1}$), Al$_2$O$_3$ (2Al$^{+3}, 3O^{-2}$)

Size of $r_A$ and $r_C$ $r_A > r_C$ $r_c/r_A < 1$
Stable ceramic crystal structure

Critical or minimum $r_c/r_A$ ratio
Cation-anion contact
<table>
<thead>
<tr>
<th>Coordination Number</th>
<th>Cation - Anion Radius Ratio</th>
<th>Coordination Geometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>&lt; 0.155</td>
<td><img src="image" alt="Coordination Geometry 2" /></td>
</tr>
<tr>
<td>3</td>
<td>0.155 – 0.225</td>
<td><img src="image" alt="Coordination Geometry 3" /></td>
</tr>
<tr>
<td>4</td>
<td>0.225 – 0.414</td>
<td><img src="image" alt="Coordination Geometry 4" /></td>
</tr>
<tr>
<td>6</td>
<td>0.414 – 0.732</td>
<td><img src="image" alt="Coordination Geometry 6" /></td>
</tr>
<tr>
<td>8</td>
<td>0.732 – 1.0</td>
<td><img src="image" alt="Coordination Geometry 8" /></td>
</tr>
</tbody>
</table>
Show that the minimum cation to anion radius ratio for the coordination number 3 is 0.155

\[
\frac{r_c}{r_A} = 0.155
\]

\[
\cos \alpha = \frac{AP}{AO} = \frac{r_A}{r_c + r_A}
\]

\[
\cos \alpha = 30^\circ = \frac{\sqrt{3}}{2}
\]

\[
\frac{r_A}{r_c + r_A} = \frac{\sqrt{3}}{2}
\]

\[
\frac{r_c}{r_A} = 0.155
\]
AX-TYPE CRYSTAL STRUCTURES

Some common ceramics

Number of cations = number of anions

Coordination number is 8

This is not BCC crystal structure because (cation and anion are involved).

ZnS, CaF2, p. 389 and 390
Electron micrograph of Kaolinite crystals. They are in the form of hexagonal plates.
The silica structure is the basic structure for many ceramics, as well as glass. It has an internal arrangement consisting of pyramid (tetrahedral or four-sided) units. Four large oxygen (O) atoms surround each smaller silicon (Si) atom. When silica tetrahedrons share three corner atoms, they produce layered silicates (talc, kaolinite clay, mica).

Clay is the basic raw material for many building products such as brick and tile. When silica tetrahedrons share four corner atoms, they produce framework silicates (quartz, tridymite). Quartz is formed when the tetrahedra in this material are arranged in a regular, orderly fashion.

If silica in the molten state is cooled very slowly it crystallizes at the freezing point. But if molten silica is cooled more rapidly, the resulting solid is a disorderly arrangement which is glass.
Cement (Portland cement) is one of the main ingredients of concrete. There are a number of different grades of cement but a typical Portland cement will contain:

- 19 - 25% SiO2
- 5 - 9% Al2O3
- 60 - 64% CaO
- 2 - 4% FeO.

Cements are prepared by grinding the clays and limestone in proper proportion, firing in a kiln, and regrinding. When water is added, the minerals either decompose or combine with water, and a new phase grows throughout the mass.

The reaction is solution, re-crystallization, and precipitation of a silicate structure. It is usually important to control the amount of water to prevent an excess that would not be part of the structure and would weaken it. The heat of hydration (heat of reaction in the adsorption of water) in setting of the cement can be large and can cause damage in large structures.
Nitrides combine the superior hardness of ceramics with high thermal and mechanical stability, making them suitable for applications as cutting tools, wear-resistant parts and structural components at high temperatures. TiN has a cubic structure which is perhaps the simplest and best known of structure types. Cations and anions both lie at the nodes of separate fcc lattices. The structure is unchanged if the Ti and N atoms (lattices) are interchanged.

Ferroelectric Ceramics

Depending on the crystal structure, in some crystal lattices, the centers of the positive and negative charges do not coincide even without the application of external electric field. In this case, it is said that there exists spontaneous polarization in the crystal. When the polarization of the dielectric can be altered by an electric field, it is called ferroelectric. A typical ceramic ferroelectric is barium titanate, $\text{BaTiO}_3$. Ferroelectric materials, especially polycrystalline ceramics, are very promising for varieties of application fields such as piezoelectric/electrostrictive.
Atomic Arrangements in Ceramics

- Most ceramics are compounds of **metallic** and **non-metallic** elements.
- Interatomic bonds can range from totally **ionic** to a **combination of ionic and covalent** to totally **covalent**.
- Many ceramics have an amorphous structure—i.e. **they feature no long-range order**
  
  e.g. glasses: non-crystalline silicates (SiO₂) containing other oxides (Na₂O, CaO, K₂O, Al₂O₃)
- Many others take on crystal structures.
Ceramic Crystal Structures

- Ceramics are composed of at least two different elements,
  - crystal structures are generally more complex than those of metals.
- for predominantly ionic bonding:
  - crystal structures may be thought of as being composed of ionic rather than atoms.
  - **Cations**: positively charged metallic ions
  - **Anions**: negatively charged non-metallic ions
  - e.g.: NaCl
    - Na\(^+\) = cation
    - Cl\(^-\) = anion
CERAMIC DENSITY

For metals

$$\rho = \frac{nA}{V_c N_A}$$

For crystal ceramic material

$$\rho = \frac{n' \left( \Sigma A_c + \Sigma A_A \right)}{V_c N_A}$$

$n'$ is number of formula units within the unit cell, ex: CaF2, one ion Ca, two ions F.

$\Sigma A_c$ is the total of the atomic weight of all cations in the formula units

$\Sigma A_A$ is the total of the atomic weight of all anions in the formula units

$V_c$ is the volume of the unit cell

$N_A$ is Avogadro’s number

$6.023 \times 10^{23}$ formula units/mol

Ch. 12 Structures and Properties of Ceramics
Based on crystal structure, write the theoretical density for NaCl. How can it be compared with its measured density?

\[
\rho = \frac{n'( \Sigma A_c + \Sigma A_A )}{V_c N_A}
\]

- \( n' \) is 4 because both ions form FCC
- \( A_c = A_{Na} = 22.99 \text{ g/mol} \)
- \( \Sigma A_A = A_{Cl} = 35.45 \text{ g/mol} \)

\[
V_c = a^3 = (2r_{Cl^-} + 2r_{Na^+})^3
\]

From Table 12.3 p. 387, \( r_{Na^+} = 0.102 \text{ nm} \) and \( r_{Cl^-} = 0.181 \text{ nm} \)

\[
\rho = \frac{4 (22.99 + 35.45)}{[2(0.102\times10^{-7}) + 2(0.181\times10^{-7})]^3 \cdot (6.023\times10^{23})} = 2.14 \text{ g/cm}^3
\]

Experimental = 2.16 g/cm\(^3\)
Silicate Ceramics

These materials contain silicon and oxygen.

Crystal structure of silicate

Various arrangement of $\text{SiO}_4^{-4}$ (tetrahedron)

Often the silicates are not ionic because the covalent character is significant to Si-O bonds (51 form table 12.1)

Different silicate structures arise from different ways

$\text{SO}_4^{4-}$ Units can be combined into 1, 2 and 3 dimensional arrangements.
Silica \( \text{SiO}_2 \)

Crystal structure: 3-dimensional

The material is electrically neutral, all atoms have stable electronic structures \( \text{Si}/\text{O} = 1/2 \)

If the structure is organised, a crystalline structure is formed

3 primary polymorphic crystalline forms of silica

1. Quartz, 2. cristobalite, 3. tridymite (structures are complicated)

They have low density, quartz at room temperature (2.65 g/cm\(^3\))

\( T_m \) of Si-O is 1710 °C

Silica glasses

High degree of atomic randomness (characteristics of liquid, called fused silica or vitreous silica)

\( \text{SO}_4 \) is the basic unit in the disorder

\( \text{B}_2\text{O}_3, \text{GeO}_2 \)
The silicates

Simple silicates

Ex: Mg$_2$SiO$_4$ (forsterite)

Ca$_2$MgSi$_2$O$_7$ (Akermanite)

SiO$_4^{4-}$

Si$_2$O$_7^{6-}$

Si$_3$O$_9^{7-}$

Si$_6$O$_{18}^{12-}$

(SiO$_3$)$_n^{2n-}$
Layered silicates

It is represented by \((\text{SiO}_5)^{2-}\)

These materials called the sheet or layered silicates

Ex: Clay, Kaolinite clay \(\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4\)

Tetrahedral layer is \(\text{Si}_2\text{O}_5^{2-}\)

Adjacent layer is \(\text{Al}_2(\text{OH})_4^{2+}\)

Carbon

Diamond
Graphite
Carbon nano-tubes
Imperfections in Ceramics

Atomic point defects

Impurities in Ceramics

Impurity atoms can form SS in ceramic materials as in metals

SS: substitution
Interstitial types are possible

Ex: NaCl, impurity Ca $^{2+}$ would likely substitute for Na$^+$ and O$^{2-}$ ions would likely substitute for Cl$^{-}$ ions
Mechanical properties

Brittle Fracture of Ceramics

At room temperature

Ceramics
  crystalline
  Non-crystalline

Fracture before any plastic deformation

Brittle fracture process

Formation
Propagation of cracks in cross section of ceramics

The growth of the cracks is through grains

The degree of stress amplification depends on cracks length and tip radius of curvature

\[ K_{lc} = Y \sigma \sqrt{\pi a} \]

- \( \sigma \) is applied stress
- \( Y \) is a dimensionless parameters
- \( a \) is length of surface crack