Density Calculations in Ceramic Structures

\[ \rho = \frac{n' \times (\sum A_C + \sum A_A)}{V_c \times N_A} \]

- \( n' \): number of formula units in unit cell (all ions that are included in the chemical formula of the compound = formula unit)
- \( \Sigma A_C \): sum of atomic weights of cations in the formula unit
- \( \Sigma A_A \): sum of atomic weights of anions in the formula unit
- \( V_c \): volume of the unit cell
- \( N_A \): Avogadro’s number, 6.023 \times 10^{23} \) (formula units)/mol
**Example: NaCl**

\( n' = 4 \) in FCC lattice

\[ \Sigma A_C = A_{Na} = 22.99 \text{ g/mol} \]

\[ \Sigma A_A = A_{Cl} = 35.45 \text{ g/mol} \]

\[ r_{Na} = 0.102 \times 10^{-7} \text{ cm} \]

\[ r_{Cl} = 0.181 \times 10^{-7} \text{ cm} \]

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

\[ V_c = (2 \times 0.102 \times 10^{-7} + 2 \times 0.181 \times 10^{-7})^3 \text{ cm}^3 \]

\[ \rho = \frac{4 \times (22.99 + 35.45)}{\left[2 \times 0.102 \times 10^{-7} + 2 \times 0.181 \times 10^{-7}\right]^3 \times 6.023 \times 10^{23}} = 2.14 \text{ g.cm}^{-3} \]
Silicate Ceramics

- Composed mainly of silicon and oxygen, two most abundant elements in earth’s crust (rocks, soils, clays, sand)
- Basic building block: $\text{SiO}_4^{4-}$ tetrahedron
- Si-O bonding is largely covalent, but overall $\text{SiO}_4^4$ block has charge of $-4$
- Various silicate structures – different ways to arrange $\text{SiO}_4^{-4}$ blocks

**Figure 12.9** A silicon–oxygen ($\text{SiO}_4^{4-}$) tetrahedron.
Figure 12.13  Schematic representation of the two-dimensional silicate sheet structure having a repeat unit formula of \((\text{Si}_2\text{O}_5)^{2-}\).
Carbon

Carbon is not a ceramic
Carbon exists in various polymorphic forms: \( \text{sp}^3 \) diamond, and amorphous carbon, \( \text{sp}^2 \) graphite and fullerenes/nanotubes.

**Carbon Diamond**
- Has diamond-cubic structure (like Si, Ge)
- One of the strongest/hardest material known
- High thermal conductivity
- Transparent in the visible and infrared, with high index of refraction. Semiconductor (can be doped to make electronic devices)
- Metastable (transforms to carbon when heated)

**Carbon: Graphite**
- Layered structure with strong bonding within the planar layers and weak (van der Waals) between layers
- Easy interplanar cleavage (lubricant and for writing pencils)
- Good electrical conductor
- Chemically stable even at high temperatures
- Applications include furnaces, rocket nozzles, welding electrodes.
Carbon

**Figure 12.15** A unit cell for the diamond cubic crystal structure.

**Figure 12.17** The structure of graphite.

**Figure 12.18** The structure of a $C_{60}$ molecule.

**Figure 12.19** The structure of a carbon nanotube. (Reprinted by permission from *American Scientist*, magazine of Sigma Xi, The Scientific Research Society. Illustration by Aaron Cox/American Scientist.)
Carbon: buckyballs and nanotubes

Buckminsterfullerenes (buckyballs) and carbon nanotubes are expected to play an important role in future nanotechnology applications (nanoscale materials, sensors, machines, and computers).

X-Ray Spectroscopy

Visible light: 0.4-0.7μm ~ 6000Å

Mo: 35KeV ~ 0.02-0.14nm

\[ E = h\nu = \frac{hc}{\lambda} \]
X-Ray Diffraction from a Crystal

- Electromagnetic radiation is wave-like:

- Waves can add constructively or destructively:
Diffraction of X-rays by Crystal Planes

Diffracted x-rays, in phase, produce a spot

Incoming x-rays

Particle layer 1

Particle layer 2

Undiffracted beam

\[ \lambda = \frac{d}{\sin \theta} \]
Bragg’s Law

For constructive interference

For cubic system:

\[ n \lambda = 2d_{hkl} \sin \theta \]

\[ n \lambda = D \sin \theta + E \sin \theta \]

\[ n \lambda = 2d_{hkl} \sin \theta \]

But no all planes diffract !!!

---

**Figure 3.20** Diffraction pattern for polycrystalline \( \alpha \)-iron.
Figure 3.19  Schematic diagram of an x-ray diffractometer; T = x-ray source, S = specimen, C = detector, and O = the axis around which the specimen and detector rotate.

$\lambda = 0.1542$ nm (CuK\textsubscript{\alpha} radiation)
Rules for Determining the Diffracting \{hkl\} Planes in Cubic Crystals

<table>
<thead>
<tr>
<th>Bravais lattice</th>
<th>Reflections present</th>
<th>Reflections absent</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td>((h + k + l) = \text{even}) ((h, k, l) \text{ all odd or all even})</td>
<td>((h + k + l) = \text{odd}) ((h, k, l) \text{ not all odd or all even})</td>
</tr>
<tr>
<td>FCC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Miller Indices of the Diffracting Planes for BCC and FCC Lattices

<table>
<thead>
<tr>
<th>Cubic planes {hkl}</th>
<th>(h^2 + k^2 + l^2)</th>
<th>(\Sigma(h^2 + k^2 + l^2))</th>
<th>FCC</th>
<th>BCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>{100}</td>
<td>1(^2) + 0(^2) + 0(^2)</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>{110}</td>
<td>1(^2) + 1(^2) + 0(^2)</td>
<td>2</td>
<td></td>
<td>110</td>
</tr>
<tr>
<td>{111}</td>
<td>1(^2) + 1(^2) + 1(^2)</td>
<td>3</td>
<td>111</td>
<td></td>
</tr>
<tr>
<td>{200}</td>
<td>2(^2) + 0(^2) + 0(^2)</td>
<td>4</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>{210}</td>
<td>2(^2) + 1(^2) + 0(^2)</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>{211}</td>
<td>2(^2) + 1(^2) + 1(^2)</td>
<td>6</td>
<td></td>
<td>211</td>
</tr>
<tr>
<td>\ldots</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>{220}</td>
<td>2(^2) + 2(^2) + 0(^2)</td>
<td>8</td>
<td>220</td>
<td>220</td>
</tr>
<tr>
<td>{221}</td>
<td>2(^2) + 2(^2) + 1(^2)</td>
<td>9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>{310}</td>
<td>3(^2) + 1(^2) + 0(^2)</td>
<td>10</td>
<td></td>
<td>310</td>
</tr>
</tbody>
</table>

For the BCC structure the first two sets of principal diffracting planes are \{110\} and \{200\}.

For the FCC structure the first two sets of principal diffracting planes are \{111\} and \{200\}.

\[
\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = \frac{h_A^2 + k_A^2 + l_A^2}{h_B^2 + k_B^2 + l_B^2}
\]

\[
\frac{\sin^2 \theta_A}{\sin^2 \theta_B} = 0.5 \text{ (BCC)}; = 0.75 \text{ (FCC)}
\]
Ex: An element, BCC or FCC, shows diffraction peaks at 2θ: 40, 58, 73, 100.4 and 114.7.

Determine:

(a) Crystal structure?
(b) Lattice constant?
(c) What is the element?