# Chapter 12: Structures of Ceramics

**Outline**

- **Introduction**
- **Crystal structures**
  - Ceramic structure
  - AX-type crystal structures
  - $A_mX_p$-type
  - $A_mB_nX_p$- type
- **Silicate ceramics**
- **Carbon**

# Ceramics

- **Two or more different elements**
- **More complex than metal structures**
- **Ionic and/or covalent bonds**
- **A mix of ionic and covalent bonds - -electronegativity**
- **Ionic bonds form ions**
  - Metals donate electrons --metallic ions- -cations--positively charged
  - Non-metals gain electrons --nonmetallic ions--anions--negatively charged
- **Crystals must be electrically neutral, e.g. $CaF_2$**

# Ceramic Bonding

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

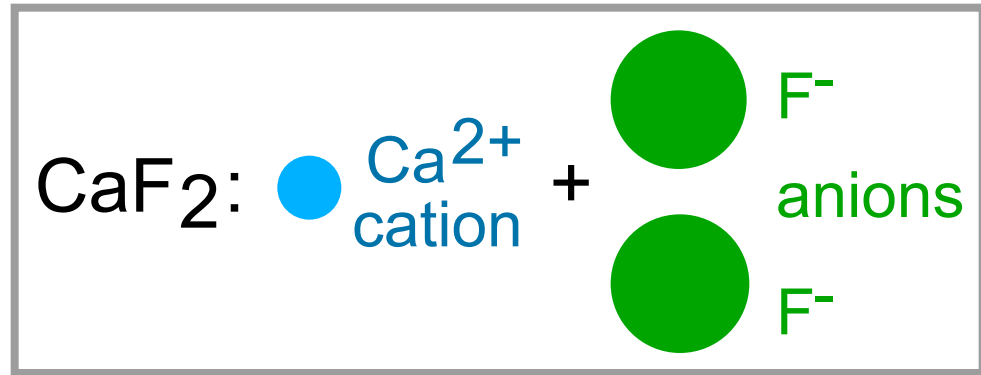- Large vs small ionic bond character:



CaF$_2$: large

SiC: small

Adapted from Fig. 2.7, *Callister 7e.* (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

# Ionic Bonding & Structure

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

  --General form:  $A_m X_p$

  m, p determined by charge neutrality

$CaF_2$:  $Ca^{2+}$ cation $+$  $F^-$ anions  $F^-$
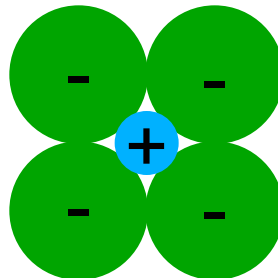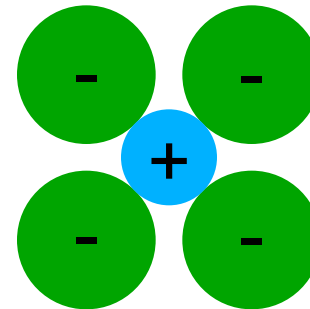
# Ceramic structures

- **Factors that influence crystal structure**

  – Magnitude of electrical charge of ions

  – Relative size of ions (Non-metal > metal ions $R_c$ /$R_a$<1)

    - **Cations must be next to anions--maximize # of nearest neighbors that are anions**

    - **Stable structure--anions and cations must contact each other**
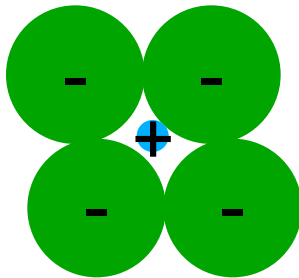


unstable          stable          stable

Adapted from Fig. 12.1, *Callister 7e.*

**The # of anions depends on ratio of $R_c$/$R_a$**

# Coordination numbers and geometries for various cation-anion radius ratios ($R_c/R_a$)

**Table 13.2** Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios ($r_C/r_A$)
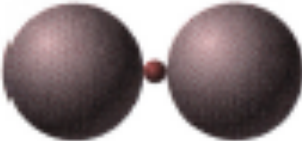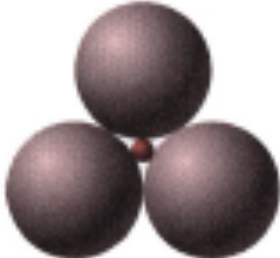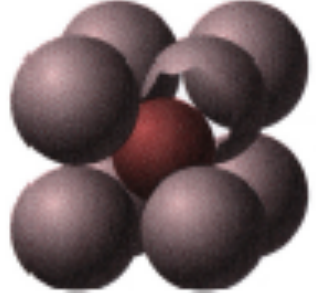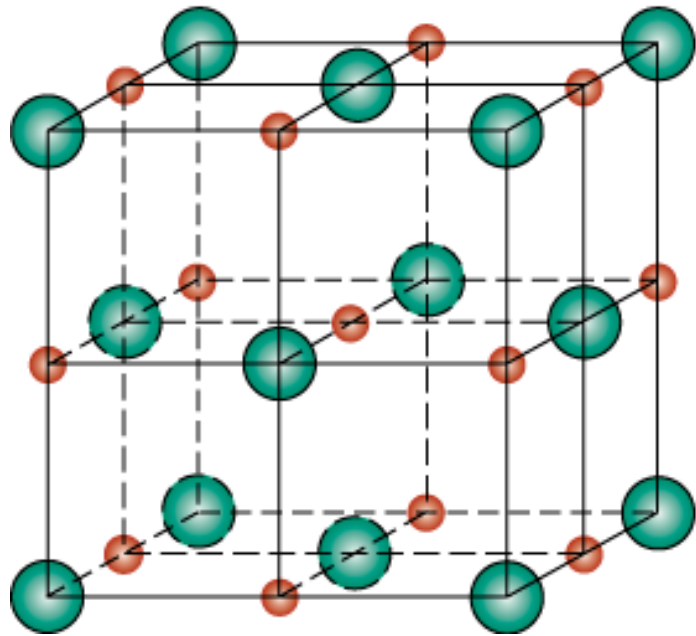
| Coordination Number | Cation–Anion Radius Ratio | Coordination Geometry |
|---|---|---|
| 2 | <0.155 | |
| 3 | 0.155–0.225 | |
| 4 | 0.225–0.414 | |
| 6 | 0.414–0.732 | |
| 8 | 0.732–1.0 | |

# AX-type crystal structure

## Rock Salt
## NaCl structure



Adapted from Fig.
12.2, *Callister 7e.*

● Na+

● Cl−

$r_{Na}$ = 0.102 nm

$r_{Cl}$ = 0.181 nm
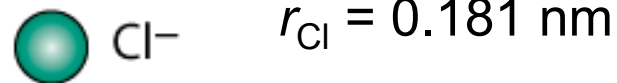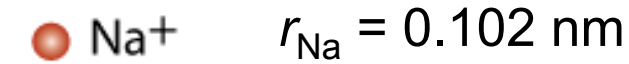
$r_{Na}/r_{Cl}$ = 0.564

C # =

Unit cell: FCC arrangement
of anions with one cation at
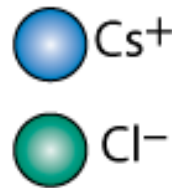center of each of 12 cube
edges
Two interpenetrating FCC
lattices

# AX Crystal Structures

AX–Type Crystal Structures include NaCl, CsCl, and zinc blende

Cesium Chloride structure:
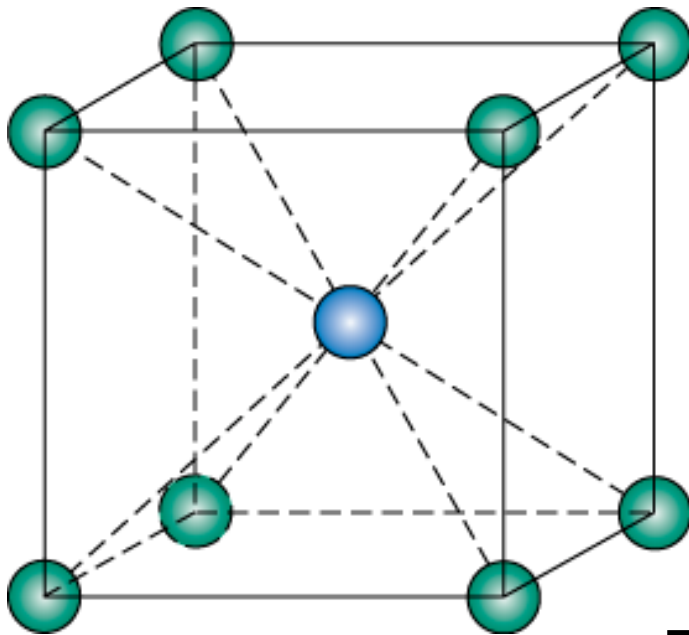


$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

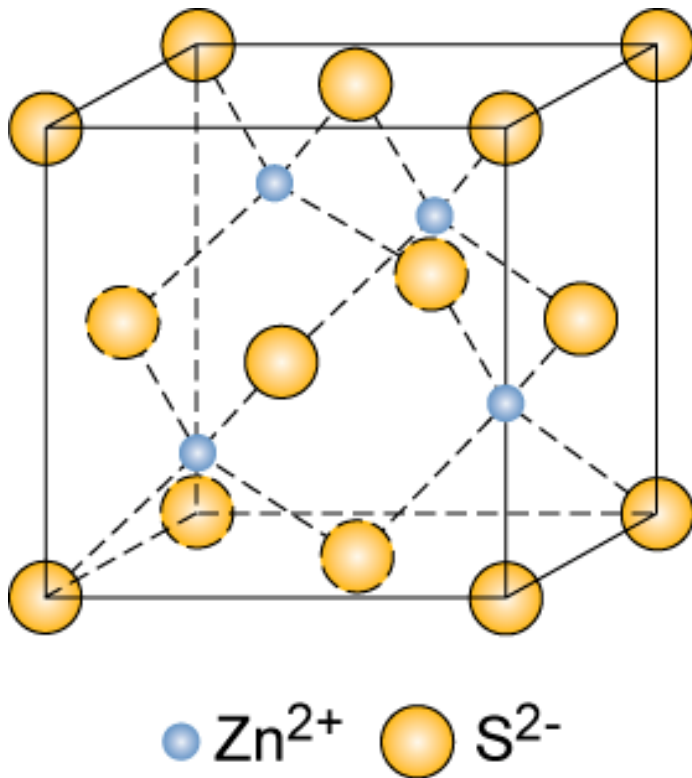Each Cs$^+$ has 8 neighboring Cl$^-$

# AX Crystal Structures

**Zinc Blende** structure



$$\frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.074}{0.140} = 0.529$$

C#=4,
FCC structure of S with Zn at interior tetrahedral

Zn$^{2+}$   S$^{2-}$

Ex: ZnO, ZnS, SiC

# $A_mX_p$ Crystal Structures

Fluorite structure ($AX_2$)



○ $Ca^{2+}$     ● $F^-$
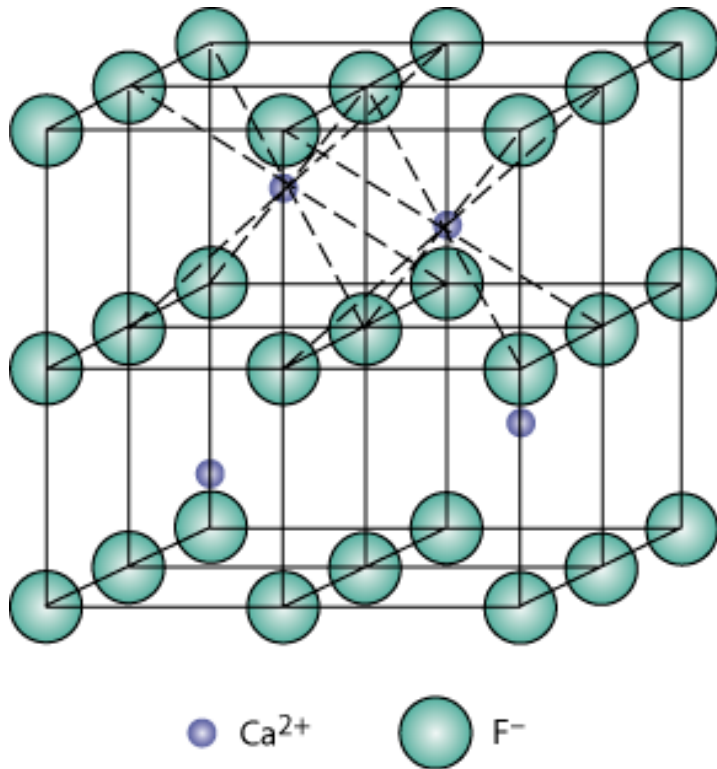
Adapted from Fig.
12.5, *Callister 7e.*

- Calcium Fluorite ($CaF_2$)

- cations in cubic sites

- $UO_2$, $ThO_2$, $ZrO_2$, $CeO_2$

- Rc/Ra=0.8, C #$_{Ca}$=8, C#$_F$=4

- Ca atoms at center of cubes with F atoms at cube corners.

- Unit cell consists of 8 cubes

# A$_m$B$_n$ X$_p$ Crystal Structures

## Perosvkite (ABX$_3$)

- **Ba at cubic corner, O at center of 6 faces, Ti at body center**

- **CN$_O$=12, CN$_{Ba}$=6, and CN $_{Ti}$=6**

- **Large A cation and oxygen form an FCC lattice**

- **Cubic--tetragonal at 130$^0$C (Curie points)**

- **Cubic -- orthrhombic and rhombohedral at low T**



● Ti$^{4+}$   ● Ba$^{2+}$   ● O$^{2-}$
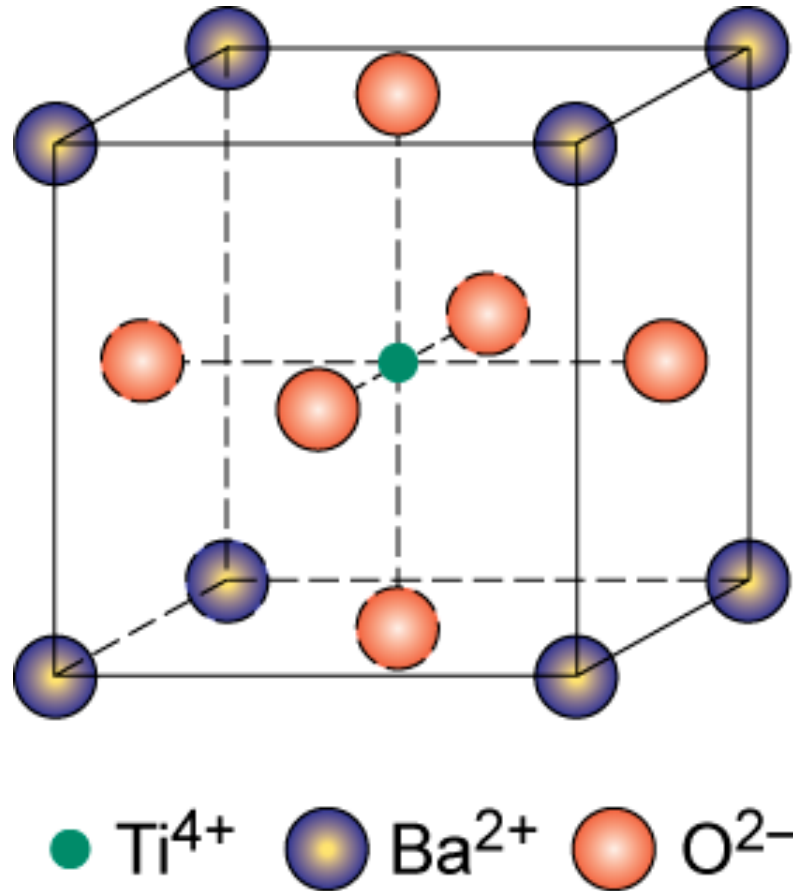
Adapted from Fig. 12.6, *Callister 7e.*

# Ceramic density computations

$$\rho = \frac{n'(\Sigma A_C + \Sigma A_A)}{V_C N_A}$$  (13.1)

where

$n'$ = the number of formula units[1] within the unit cell

$\Sigma A_C$ = the sum of the atomic weights of all cations in the formula unit

$\Sigma A_A$ = the sum of the atomic weights of all anions in the formula unit
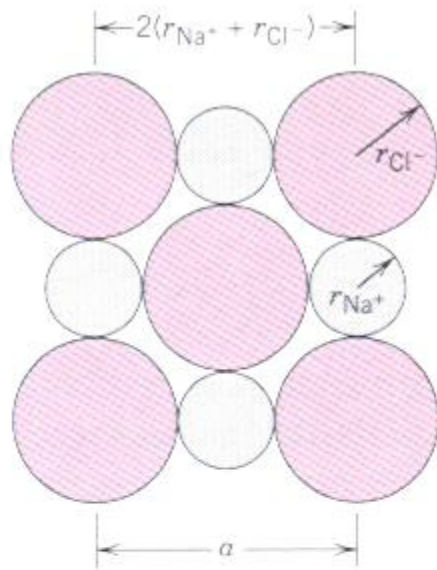
$V_C$ = the unit cell volume

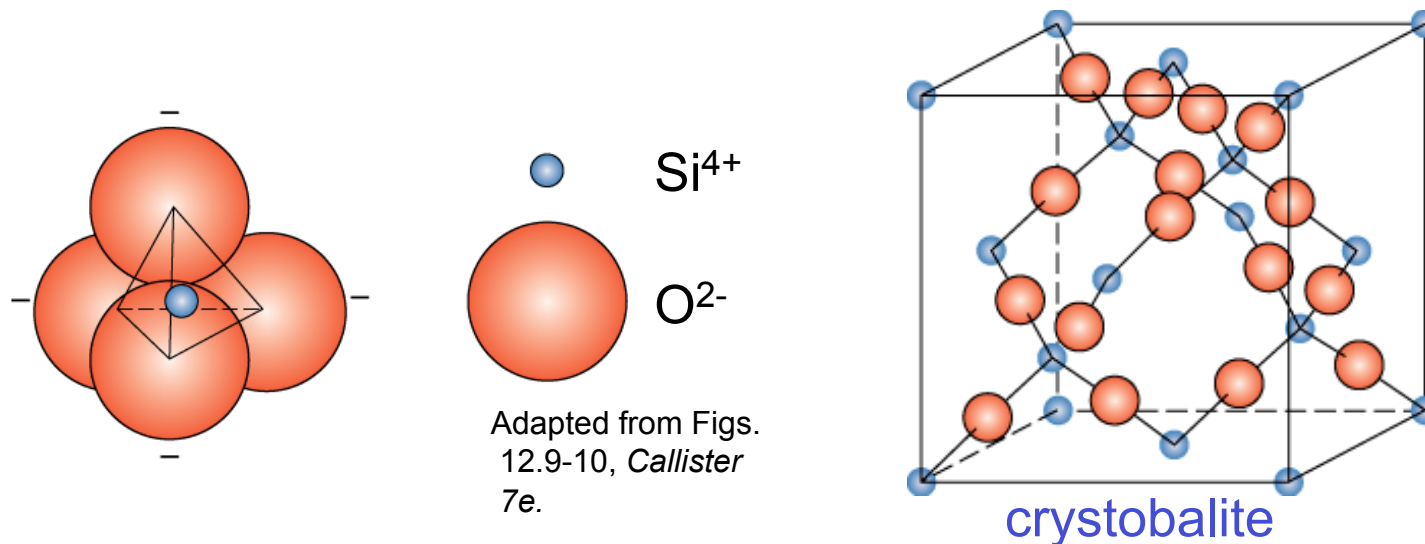$N_A$ = Avogadro's number, $6.023 \times 10^{23}$ formula units/mol

# Ceramic density computation
## (example Rock Salt)

# Silicate Ceramics

Most common elements on earth are Si & O



Si$^{4+}$

O$^{2-}$

Adapted from Figs. 12.9-10, *Callister 7e.*

crystobalite

- SiO$_2$ (silica) structures are quartz, crystobalite, & tridymite

- The strong Si-O bond leads to a strong, high melting material (1710ºC)

# Amorphous Silica

- Silica gels - amorphous $SiO_2$
    - $Si^{4+}$ and $O^{2-}$ not in well-ordered lattice
    - Charge balanced by $H^+$ (to form $OH^-$) at "dangling" bonds
        - very high surface area > 200 $m^2$/g
    - $SiO_2$ is quite stable, therefore unreactive
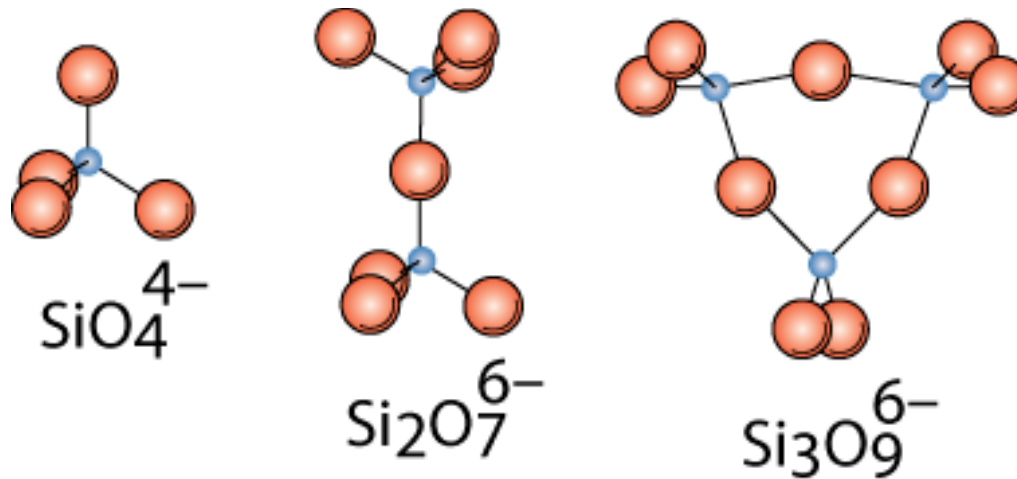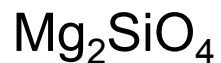        - makes good catalyst support
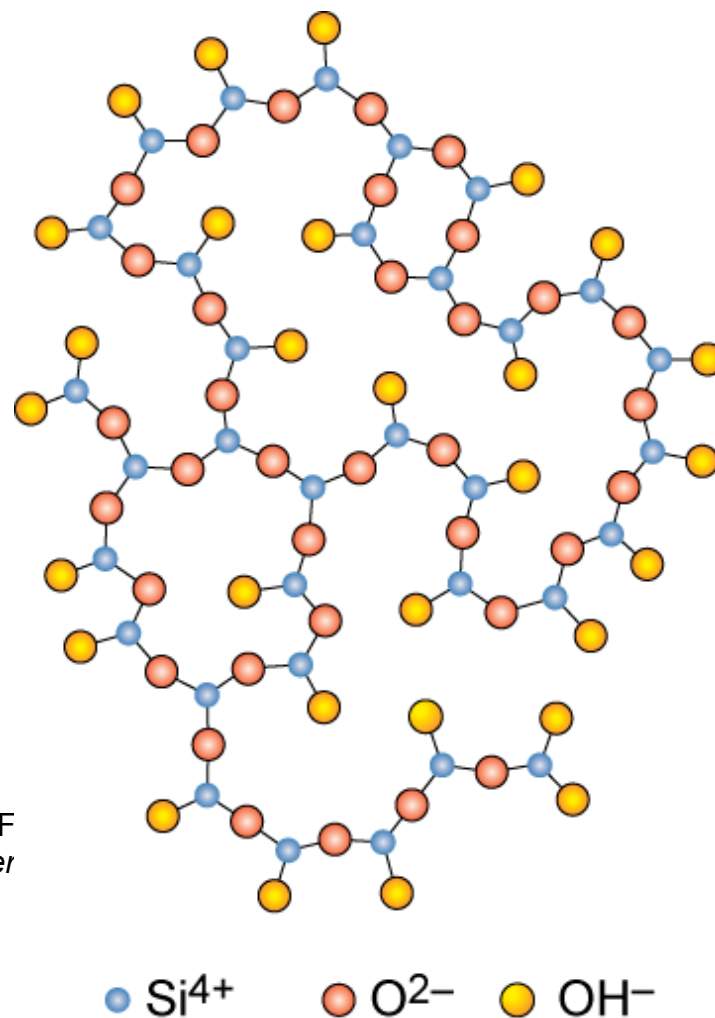
Adapted from F 12.11, *Callister*



Legend: $Si^{4+}$   $O^{2-}$   $OH^-$

# Silicates

– Combine $SiO_4^{4-}$ tetrahedra by having them share corners, edges, or faces



$SiO_4^{4-}$

$Si_2O_7^{6-}$

$Si_3O_9^{6-}$

Adapted from Fig. 12.12, *Callister 7e.*
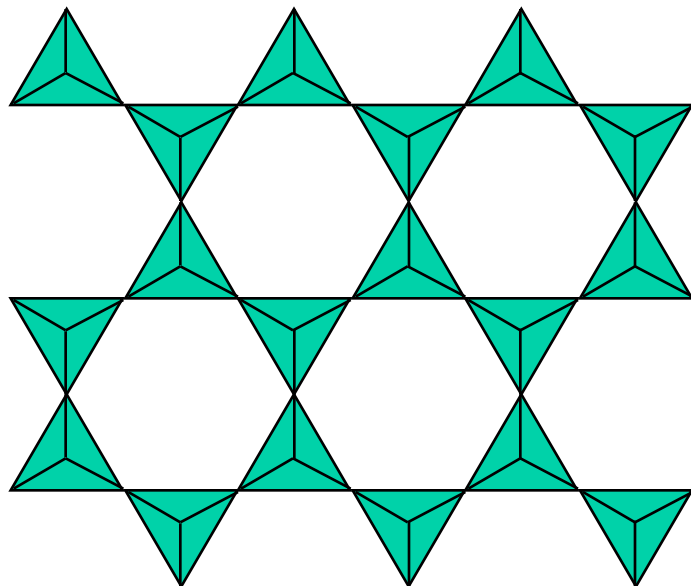
$Mg_2SiO_4$  $Ca_2MgSi_2O_7$

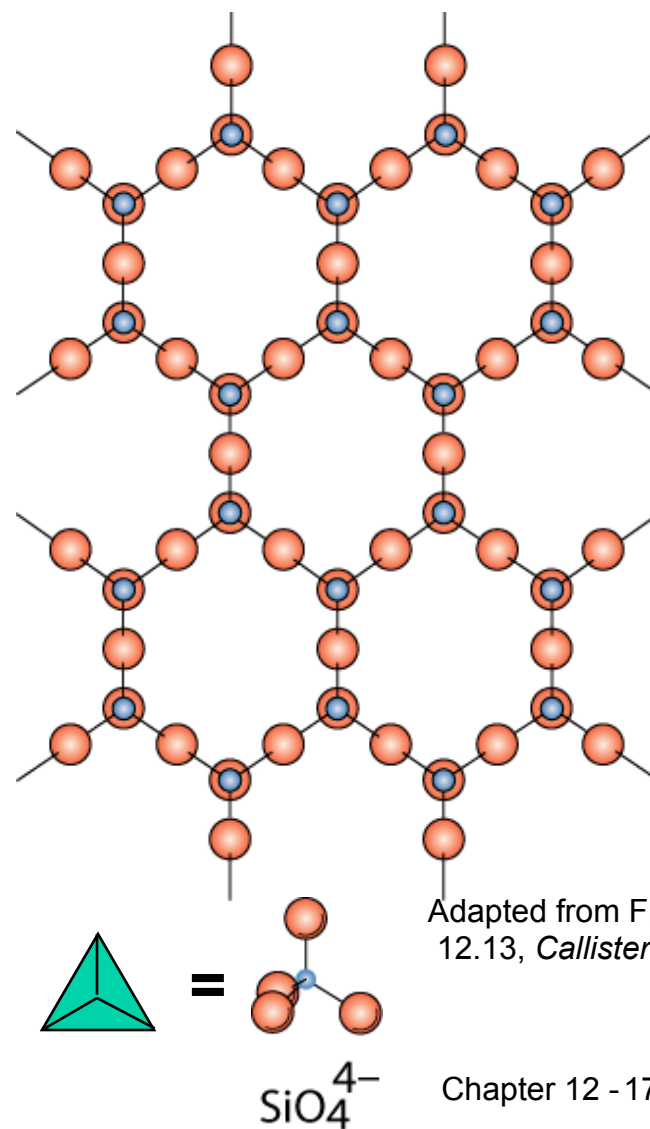– Cations such as $Ca^{2+}$, $Mg^{2+}$, & $Al^{3+}$ act to neutralize & provide ionic bonding

# Layered Silicates

- Layered silicates (clay silicates)
  - $SiO_4$ tetrahedra connected together to form 2-D plane



- $(Si_2O_5)^{2-}$
- So need cations to balance charge



$$SiO_4^{4-}$$

Adapted from Fig. 12.13, *Callister 7e.*

# Carbon Forms

- Carbon black – amorphous – surface area ca. 1000 m$^2$/g

- Diamond

  – tetrahedral carbon

    - hard – no good slip planes
    - brittle – can cut it

  – large diamonds – jewelry

  – small diamonds

    - often man made - used for cutting tools and polishing

  – diamond films
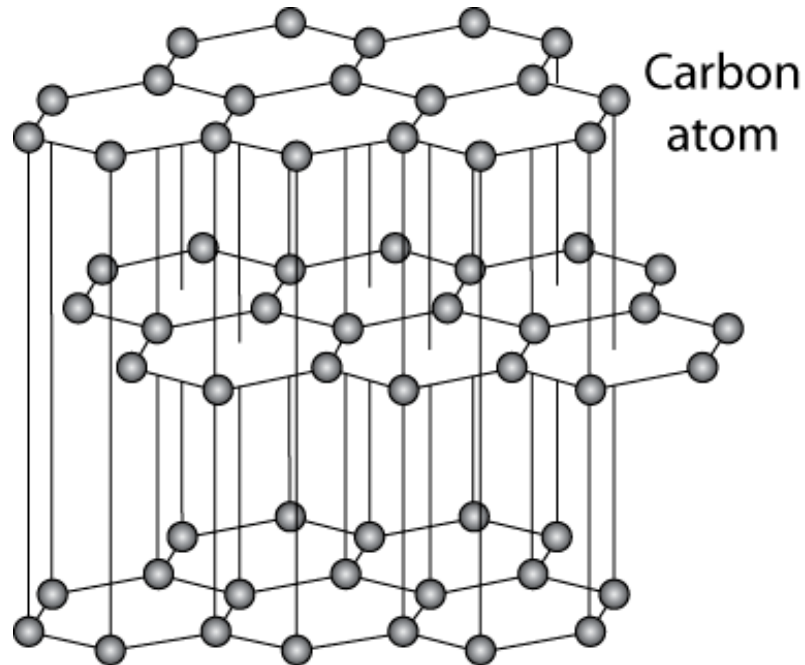
    - hard surface coat – tools, medical devices, etc.
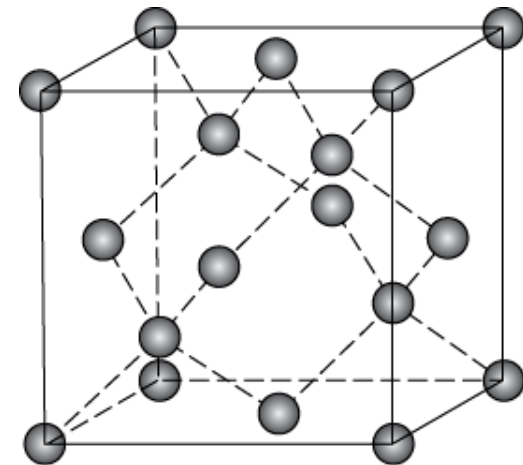
Adapted from Fig. 12.15, *Callister 7e.*

# Carbon Forms - Graphite
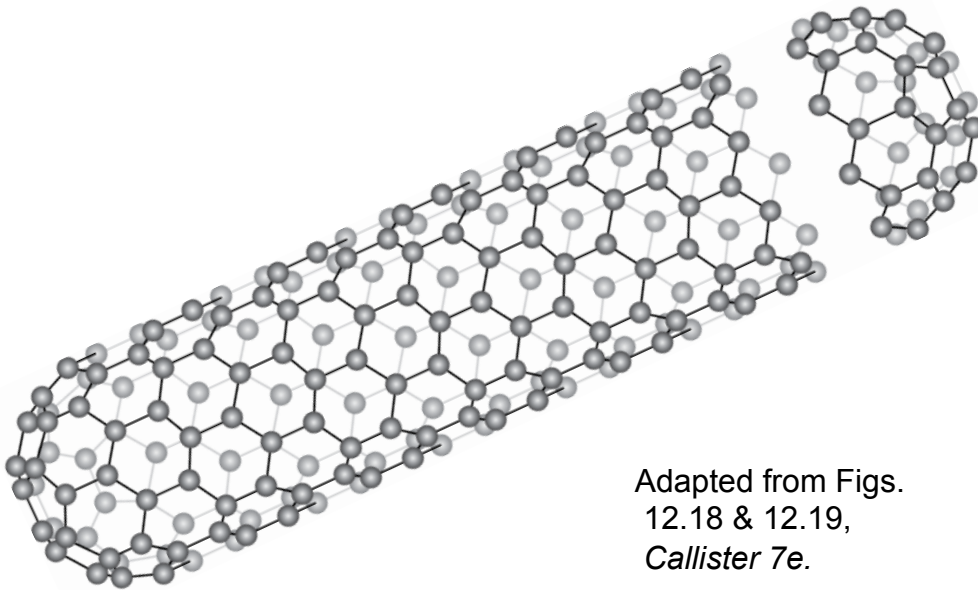
- layer structure – aromatic layers



Carbon atom

Adapted from Fig. 12.17, *Callister 7e.*

– weak van der Waal's forces between layers
– planes slide easily, good lubricant

# Carbon Forms –
# Fullerenes and Nanotubes

- Fullerenes or carbon nanotubes
  - wrap the graphite sheet by curving into ball or tube
  - Buckminister fullerenes
    - Like a soccer ball $C_{60}$ - also $C_{70}$ + others



Adapted from Figs.
12.18 & 12.19,
*Callister 7e.*