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Chapter 12: Structures of Ceramics

Outline

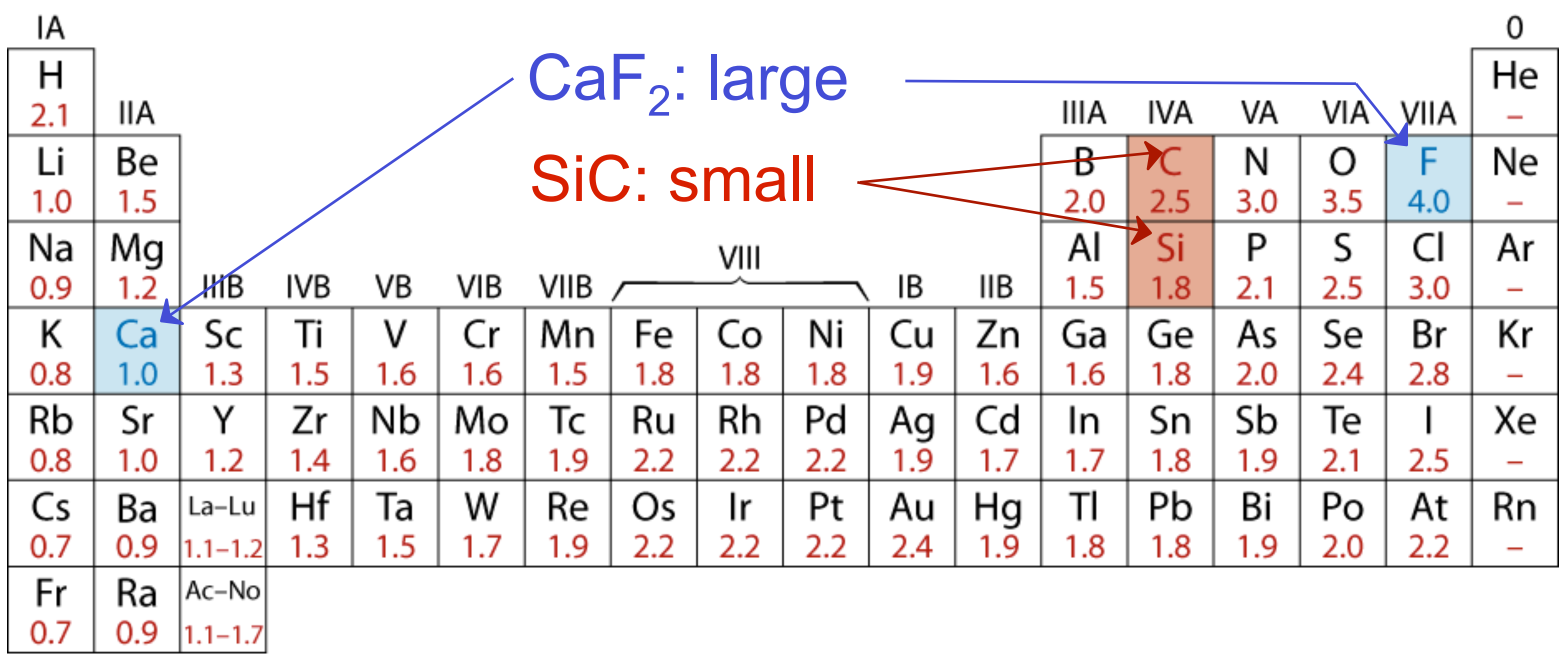
- **Introduction**
- **Crystal structures**
  - Ceramic structure
  - AX-type crystal structures
  - A_mX_p-type
  - $A_mB_nX_p$- type
- **Silicate ceramics**
- **Carbon**

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

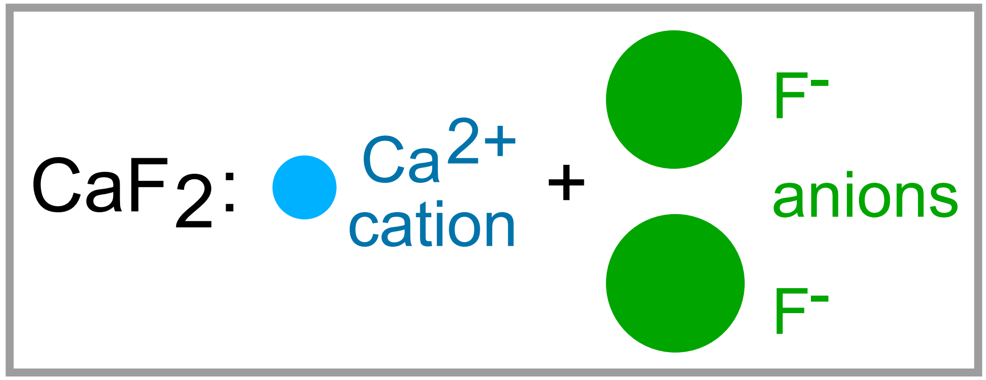
- Bonding:
  -- Mostly ionic, some covalent.
  -- % ionic character increases with difference in electronegativity.
- Large vs small ionic bond character:



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.

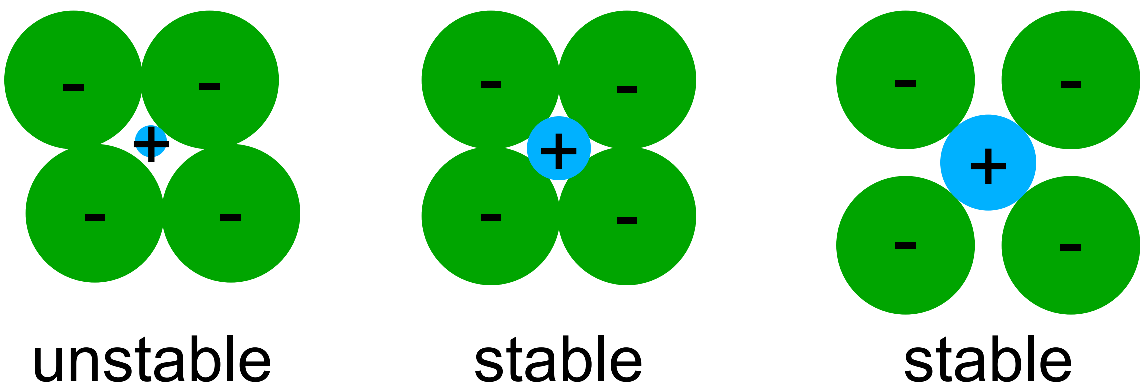


--General form: $A_m X_p$

m, p determined by charge neutrality

Ceramic structures

- **Factors that influence crystal structure**
  - Magnitude of electrical charge of ions
  - Relative size of ions (Non-metal > metal ions Rc/ Ra<1)
    - **Cations must be next to anions--maximize # of nearest neighbors that are anions**
    - **Stable structure--anions and cations must contact each other**

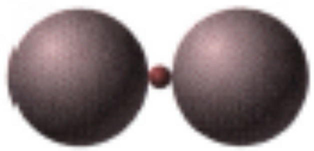
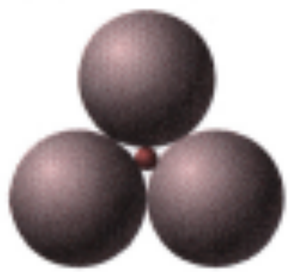
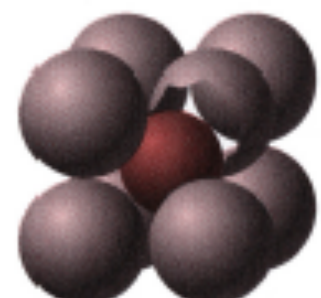


Adapted from Fig. 12.1, *Callister 7e.*

The # of anions depends on ratio of Rc/Ra

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

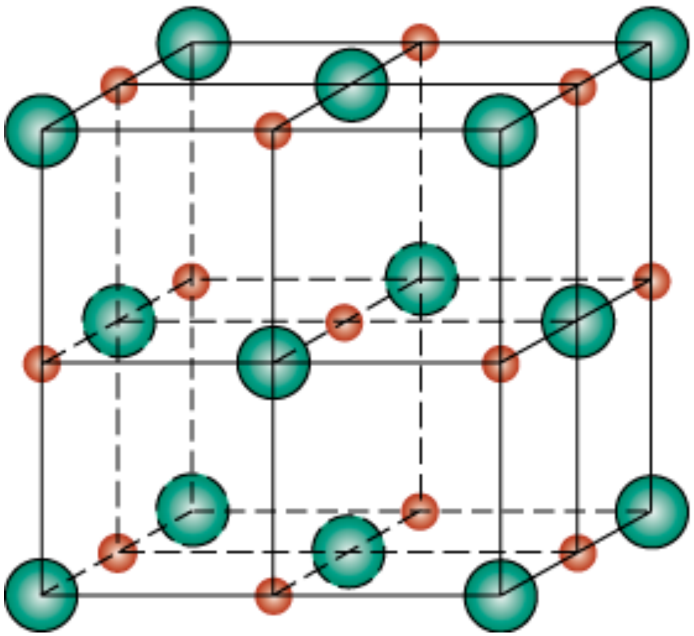
Table 13.2 Coordination Numbers and Geometries for Various Cation–Anion Radius Ratios (r_C/r_A)

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	

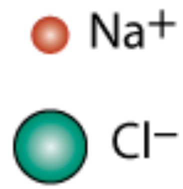
AX-type crystal structure

Rock Salt

NaCl structure



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



r_{Na} = 0.102 nm

r_{Cl} = 0.181 nm

r_{Na}/r_{Cl} = 0.564

C # =

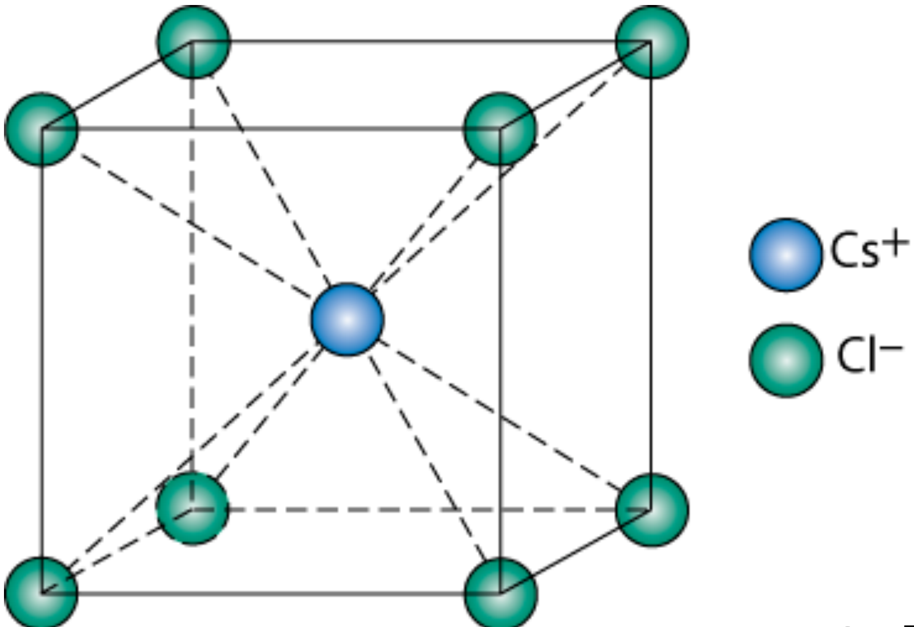
Unit cell: FCC arrangement of anions with one cation at center of each of 12 cube edges

Two interpenetrating FCC lattices

AX Crystal Structures

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

Cesium Chloride structure:



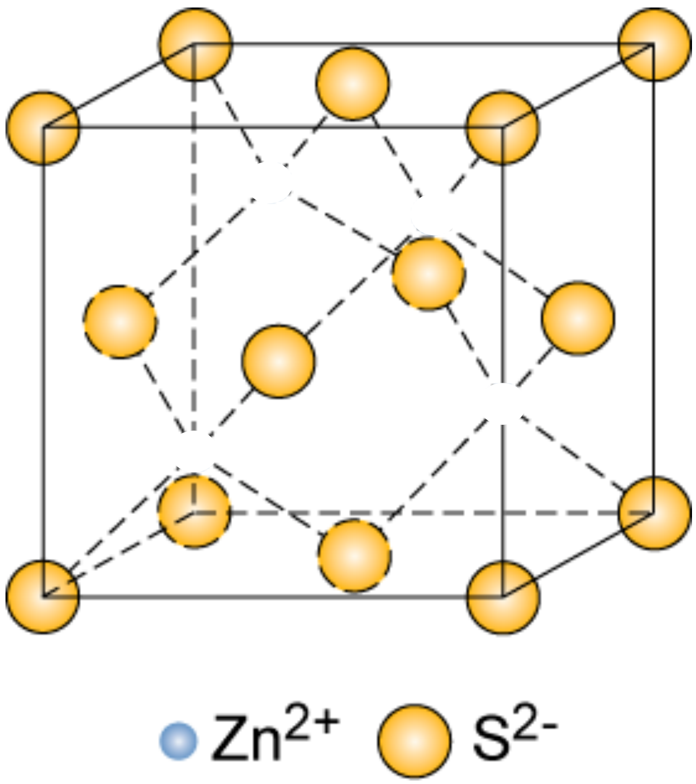
$$\frac{r_{Cs^+}}{r_{Cl^-}} = \frac{0.170}{0.181} = 0.939$$

Each Cs^+ has 8 neighboring Cl^-

Adapted from Fig. 12.3, *Callister 7e.*

AX Crystal Structures

Zinc Blende structure



Adapted from Fig. 12.4, *Callister 7e.*

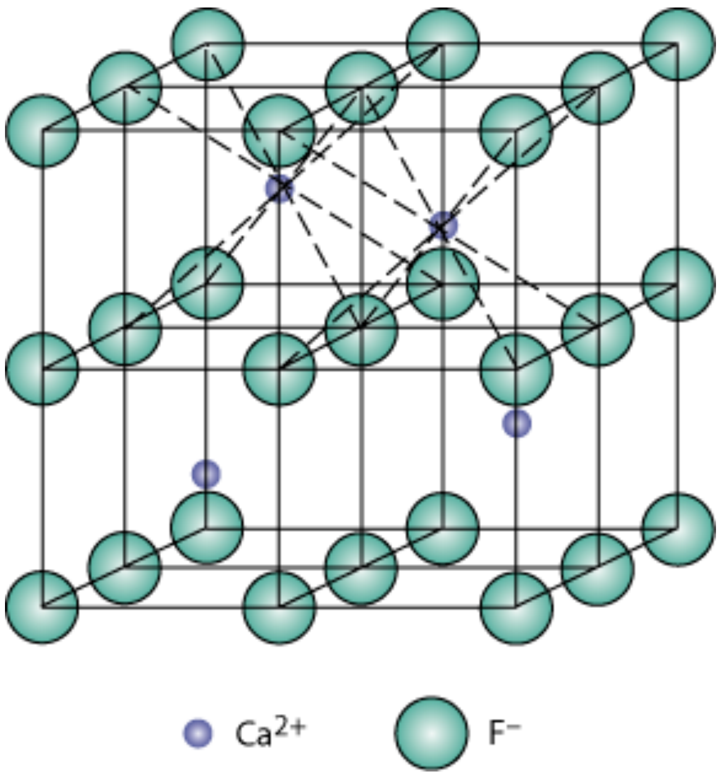
$$\frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.074}{0.140} = 0.529$$

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

Ex: ZnO, ZnS, SiC

A_mX_p Crystal Structures

Fluorite structure (AX_2)



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

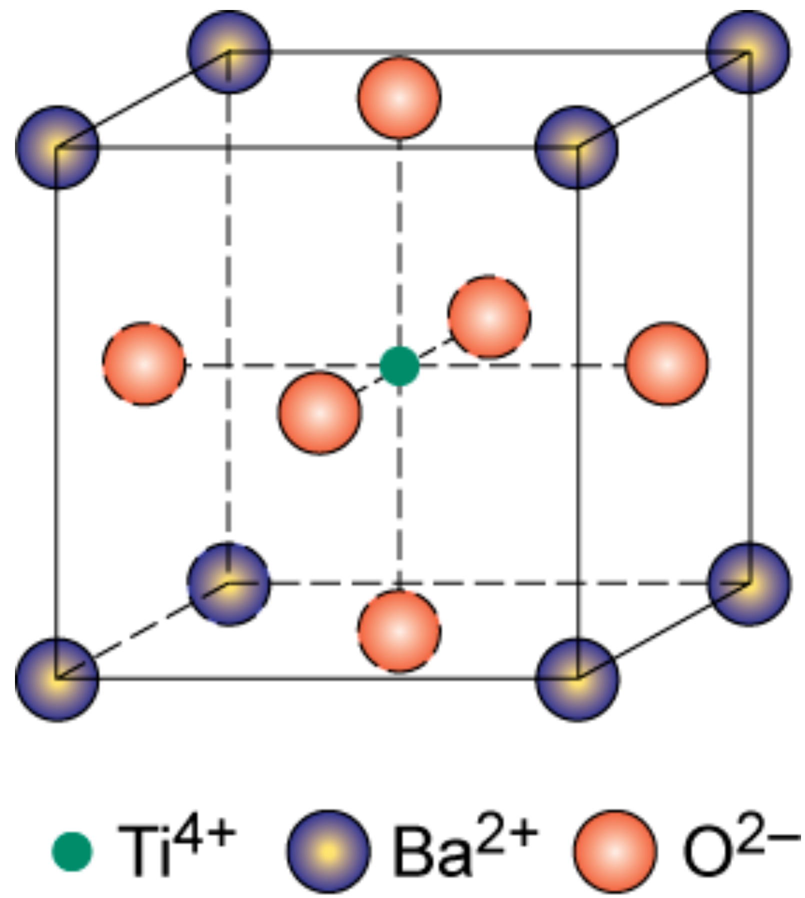
•Ca atoms at center of cubes with F atoms at cube corners.

•Unit cell consists of 8 cubes

$A_mB_n X_p$ 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**



Adapted from Fig. 12.6, *Callister 7e.*

Ceramic density computations

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

where

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

ΣA_C = the sum of the atomic weights of all cations in the formula unit

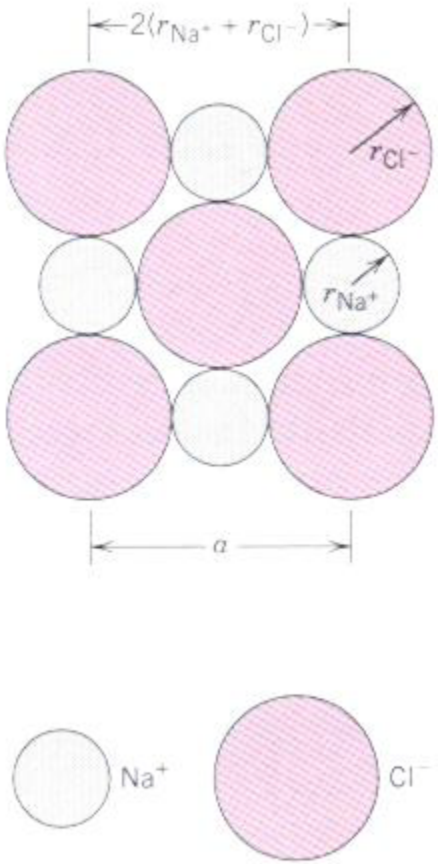
ΣA_A = the sum of the atomic weights of all anions in the formula unit

V_C = the unit cell volume

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

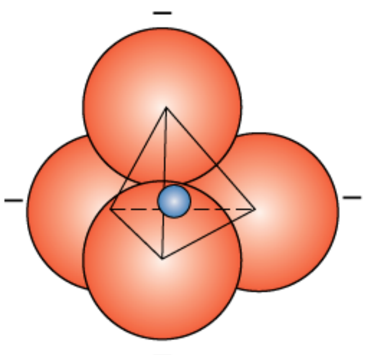
Ceramic density computation

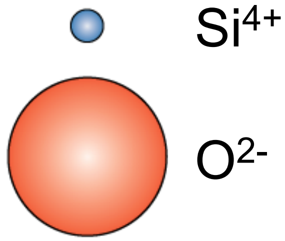
(example Rock Salt)



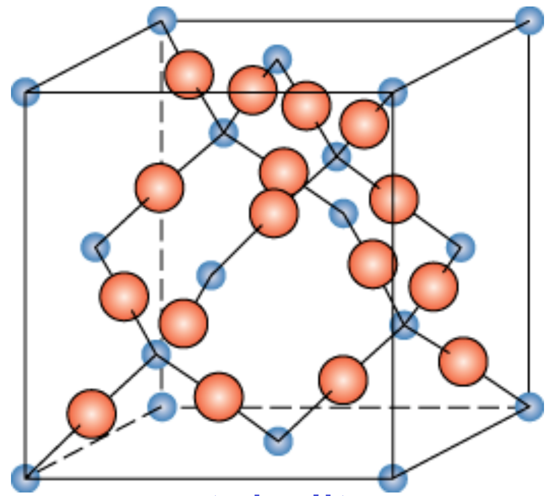
Silicate Ceramics

Most common elements on earth are Si & O





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

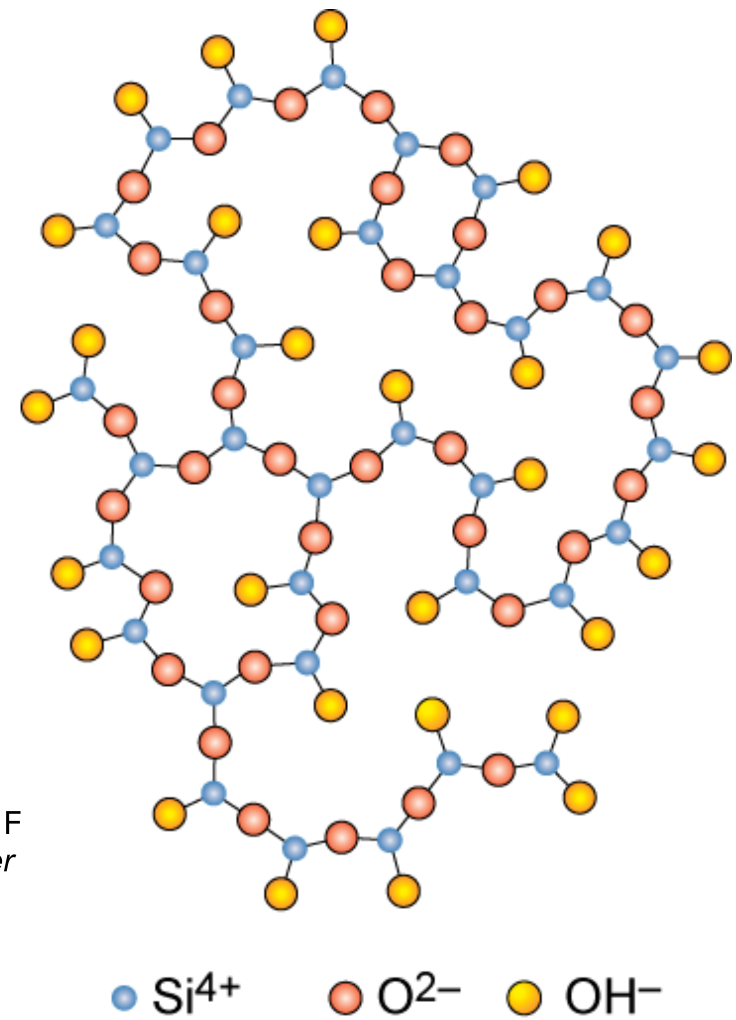


crystobalite

- SiO_2 (silica) structures are quartz, crystobalite, & tridymite
- The strong Si-O bond leads to a strong, high melting material (1710ºC)

Amorphous Silica

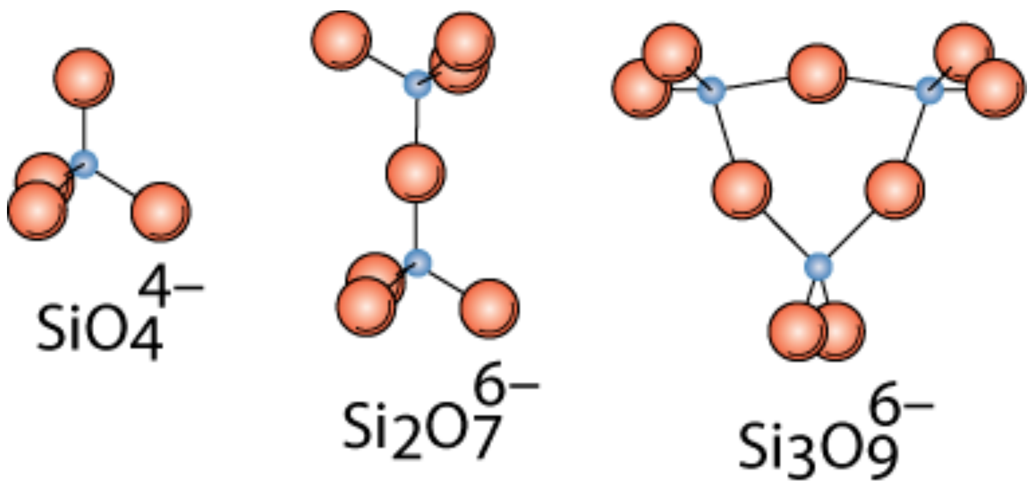
- Silica gels - amorphous SiO_2
  - Si^{4+} and O^{2-} not in well-ordered lattice
  - Charge balanced by H^+ (to form OH^-) at "dangling" bonds
    - very high surface area > 200 m^2/g
  - SiO_2 is quite stable, therefore unreactive
    - makes good catalyst support



Adapted from F 12.11, *Callister*

Silicates

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



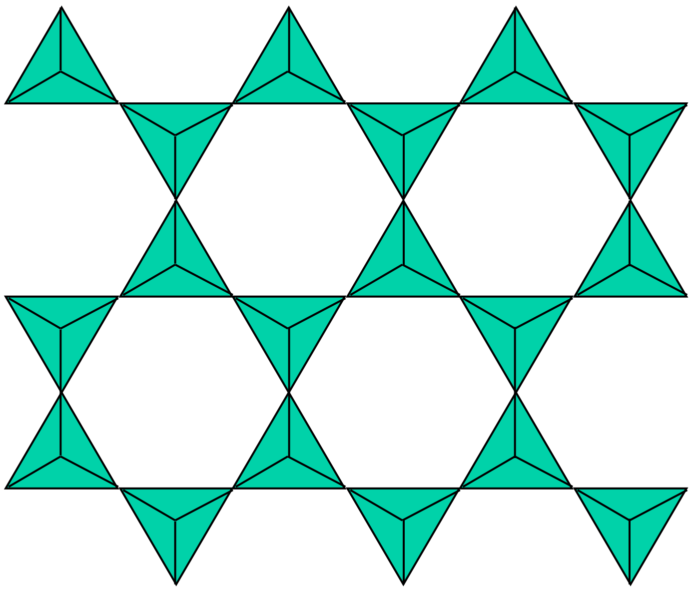
Adapted from Fig. 12.12, *Callister 7e.*

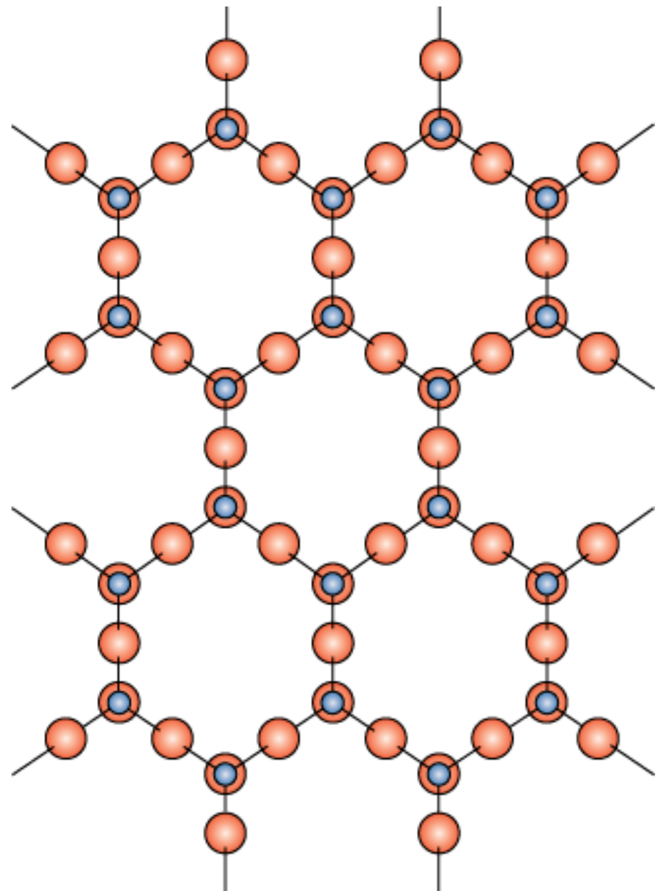
Mg_2SiO_4 $Ca_2MgSi_2O_7$

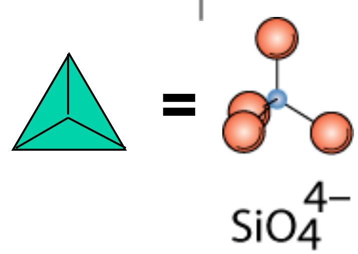
– Cations such as Ca^{2+}, Mg^{2+}, & Al^{3+} act to neutralize & provide ionic bonding

Layered Silicates

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





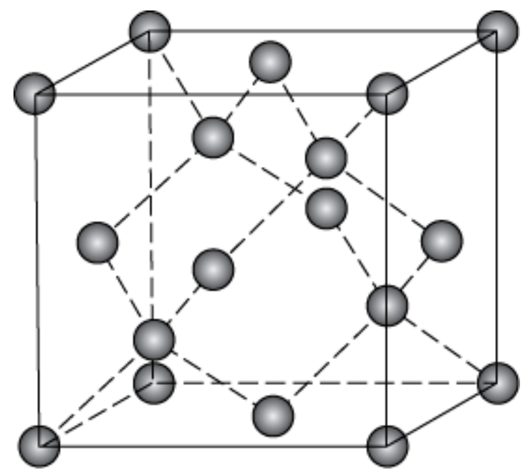


Adapted from Fig. 12.13, *Callister 7e.*

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

Carbon Forms

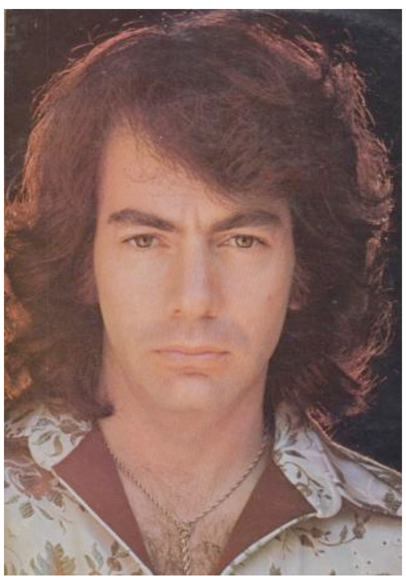
- Carbon black – amorphous – surface area ca. 1000 m^2/g
- Diamond
  - tetrahedral carbon
    - hard – no good slip planes
    - brittle – can cut it
  - large diamonds – jewelry
  - small diamonds
    - often man made - used for cutting tools and polishing
  - diamond films
    - hard surface coat – tools, medical devices, etc.



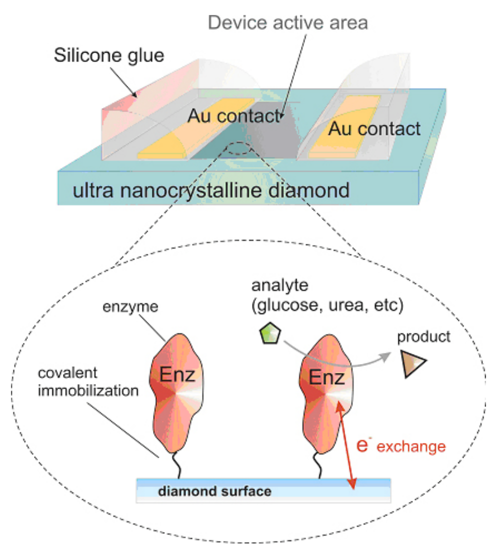
Adapted from Fig. 12.15, *Callister 7e.*

Diamonds!

100 m $

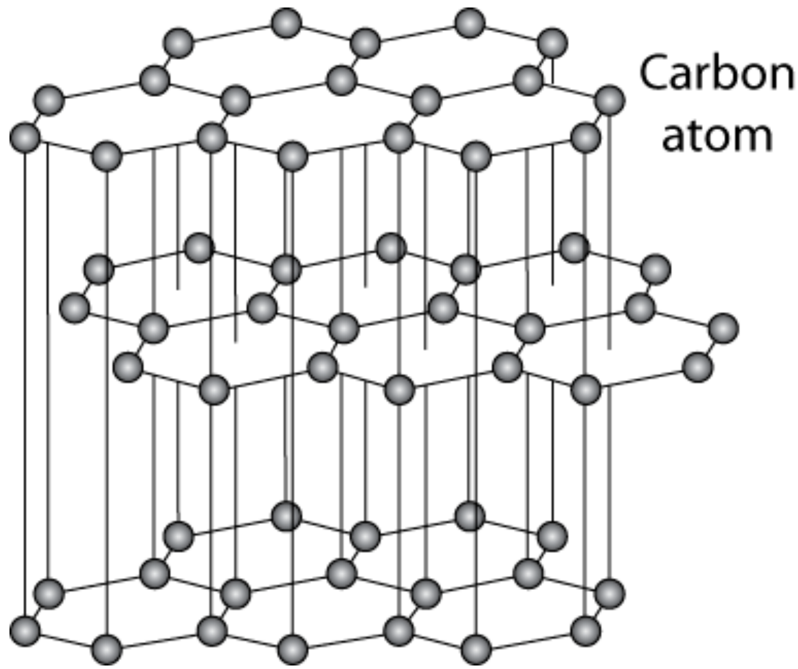


120 m



Carbon Forms - Graphite

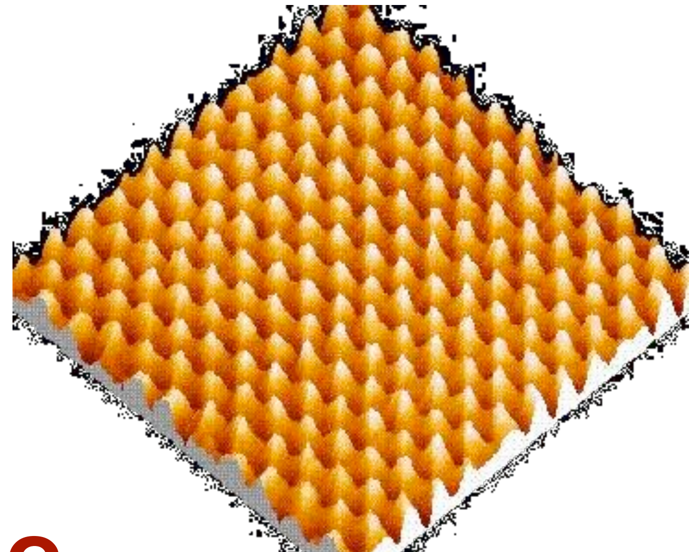
- layer structure – aromatic layers



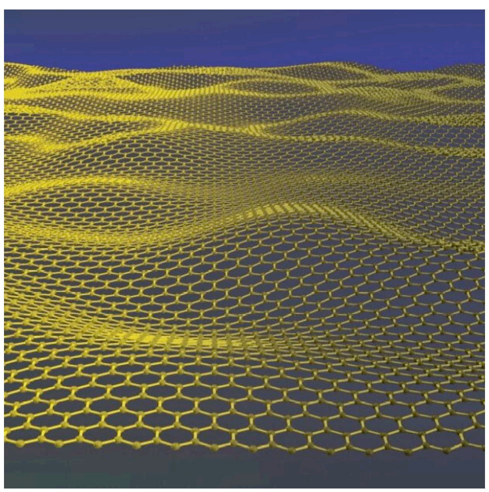
Adapted from Fig. 12.17, *Callister 7e.*

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

Graphite!

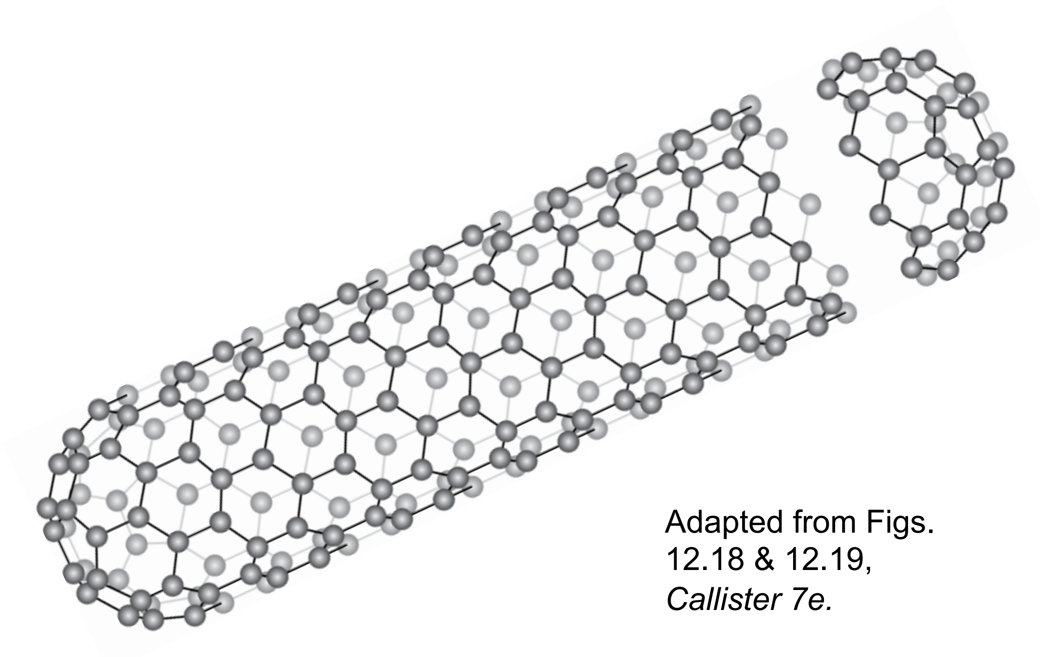


Graphene?

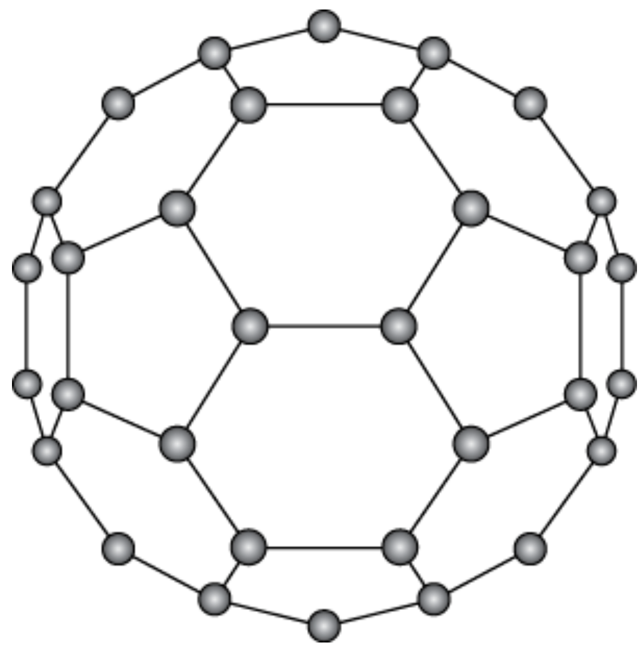


Carbon Forms – Fullerenes and Nanotubes

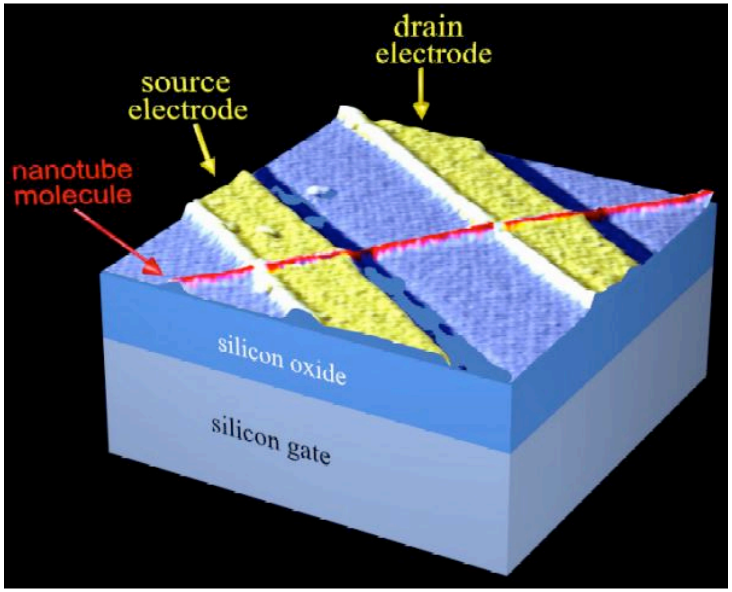
- Fullerenes or carbon nanotubes
  - wrap the graphene sheet by curving into ball or tube
  - Buckminister fullerenes
    - Like a soccer ball C_{60} - also C_{70} + others

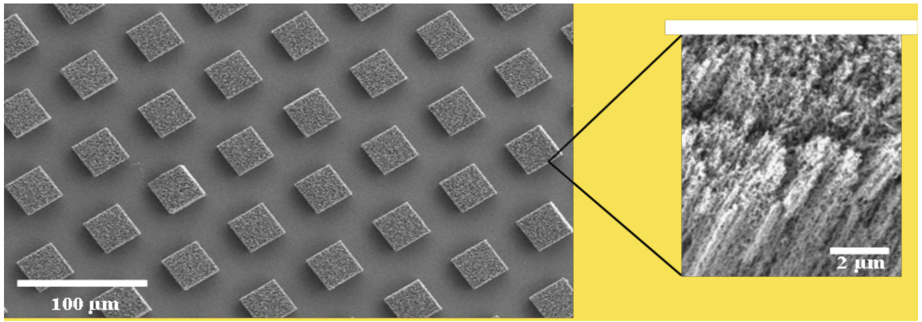


Adapted from Figs. 12.18 & 12.19, *Callister 7e.*



Nanotubes





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