Chapter 12: Structures of Ceramics

Outline

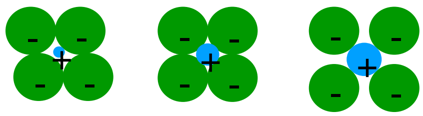
- Introduction
- Crystal structures
  - Ceramic structure
  - AX-type crystal structures
  - AmXp-type
  - AmBnXp- type
- Silicate ceramics
- Carbon

Ceramic structures

- 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 give up 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 structures (*continue*)

- Factors 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

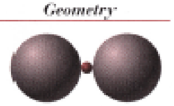
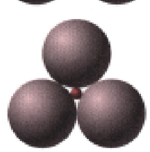
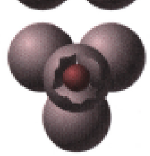


unstable stable stable

    - The # of anions depends on ratio of R_c/R_a

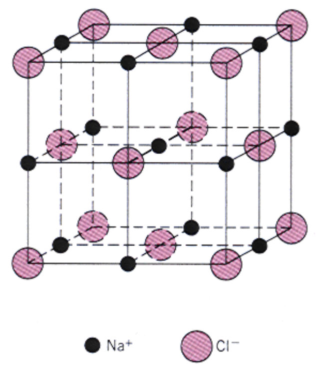
Coordination numbers and geometries for various cation-anion radius ratios (R_c/R_a)

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

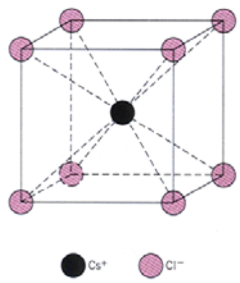
- Rock salt structure
  - Sodium chloride (NaCl) is the most common
  - Rc/Ra =0.414-0.732
  - CN=6 for both cations and anions
  - Unit cell: FCC arrangement of anions with one cation at center of each of 12 cube edges
  - Two interpenetrating FCC lattices



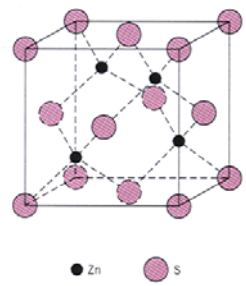
A unit cell of rock salt

AX-type crystal structure (*continue*)

- Cesium chloride structure
  - CN=8, 8 anions at cube corners and 1 cation at center of cube, simple cubic (not BCC)
- Zinc Blende structure
  - CN=4, FCC structure of S with Zn at interior tetrahedral positions



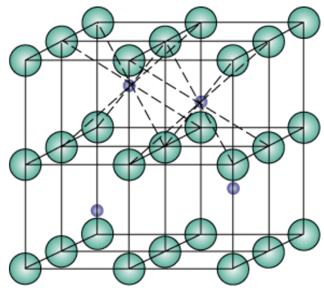
A unit cell of cesium chloride



A unit cell of zinc blende

The AmXp type crystal structures

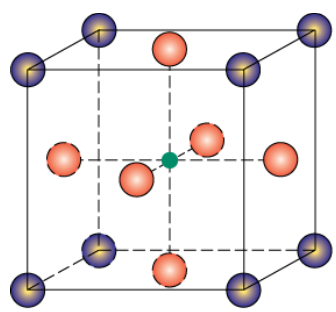
- Rc/Ra=0.8, CN_{Ca}=8, CN_F=4
- Ca atoms at center of cubes with F atoms at cube corners, similar to CsCl, but only 1/2 of sites are filled with Ca atoms
- Unit cell consists of 8 cubes



A unit cell of CaF_2 (AX2)

The AmBnXp type crystal structures

- 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



A unit cell of perovskite crystal structure (ABX3)

Example: Predicting Structure of FeO

- On the basis of ionic radii, what crystal structure would you predict for FeO?

Cation	Ionic radius (nm)
Al^{3+}	0.053
Fe^{2+}	0.077
Fe^{3+}	0.069
Ca^{2+}	0.100
Anion	
O^{2-}	0.140
Cl^{-}	0.181
F^{-}	0.133

- Answer:

$$\frac{r_{cation}}{r_{anion}} = \frac{0.077}{0.140} = 0.550$$

based on this ratio,
--coord # = 6
--structure = NaCl

Ceramic density

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

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

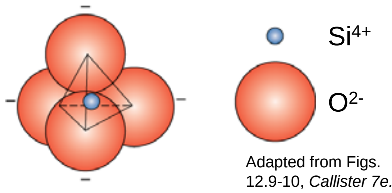
ΣA_A = the sum of the atomic weights of all anions in the formula unit

V_C = the unit cell volume

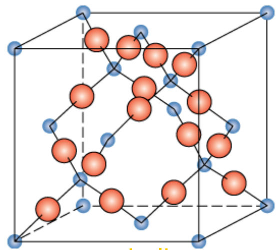
N_A = Avogadro's number, 6.023×10^{23} formula units/mol

Silicate ceramics

- Silicates are materials composed primarily of silicon and oxygen (soils, rocks, clays, sand, and glass)



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

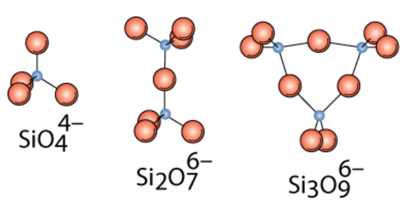


crystobalite

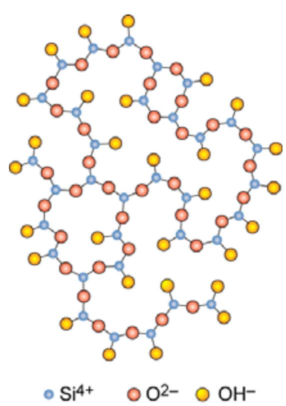
- Silica, silicon oxide (SiO_2),
  - Three crystal structures: quartz, cristobalite, and tridymite
  - Open structure, not close-packed, low density

Silicate ceramics (*continue*)

- Silica glasses
  - amorphous, a high degree of atomic randomness
  - additives, CaO and NaO, network modifier, modify the silicon and oxide network and low melting T
- The silicates



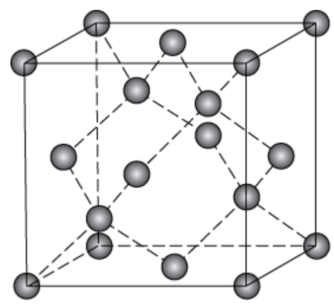
Various silicate ion structures



Sodium-silicate glass

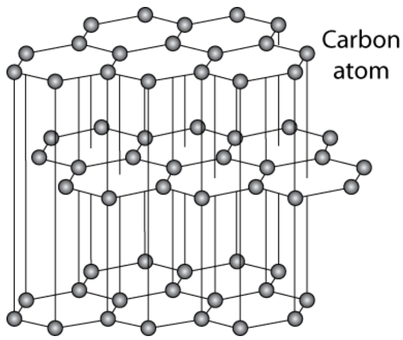
Carbon forms

- 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.



Carbon forms - graphite

- layer structure – aromatic layers

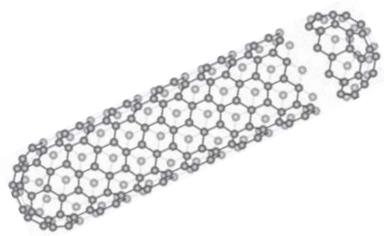


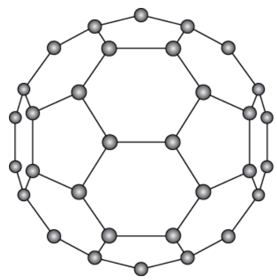
Adapted from Fig. 12.17, *Callister 7e.*

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

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





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