Earth and Planetary Materials

Spring 2013

Lecture 5
2013.01.23

Simple structures – AX

CN = 8: the CsCl structure
CN = 6: the NaCl structure
CN = 4: the wurtzite and sphalerite structures

AX structure (CN = 8)

CN = 8: the CsCl structure

- Based on a simple cubic (SC) arrangement of anions

- All the CN=8 (cubic) sites are filled
- The Cs(Cl)8 cubes share faces

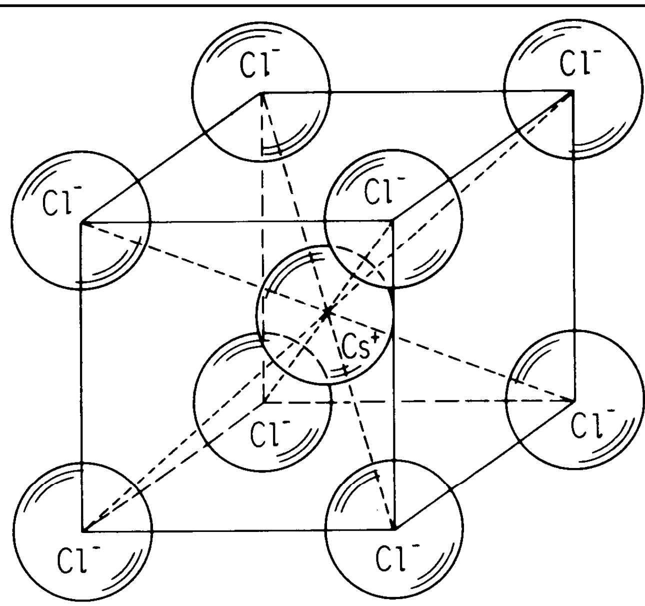


Figure 2-3 CsCl structure. This structure is made up of two interpenetrating PC lattices. The unit cell of CsCl may be shown with either Cs^+ or Cl^- in the PC positions. All ions are in cubic coordination.

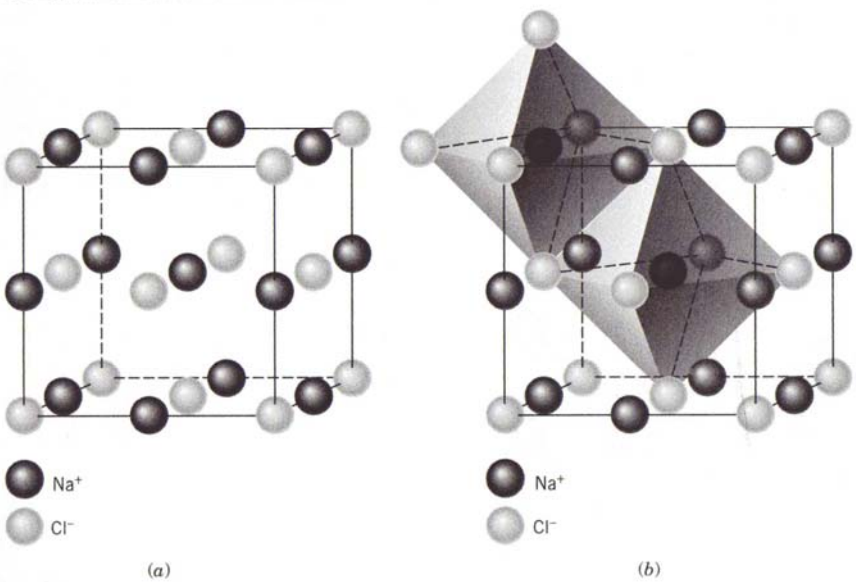
AX structure (CN = 6)

CN = 6: the NaCl structure

(halite structure, rock salt structure)

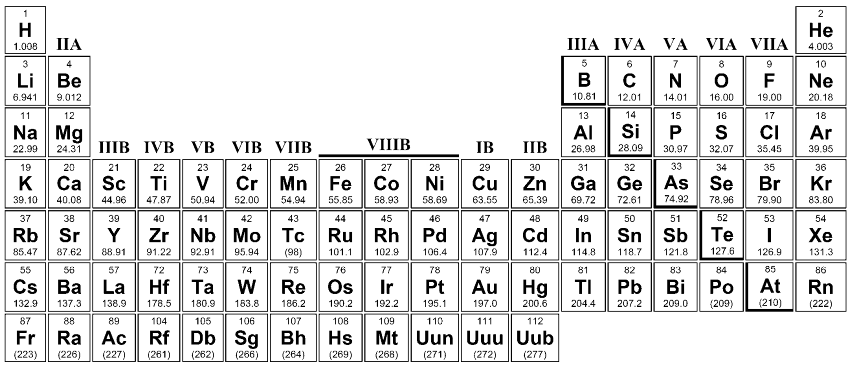
- Based on a CCP arrangement of anions, which corresponds to an FCC unit cell
- The Na(Cl)6 octahedra share edges

FIG. 4.17 (a) The structure of NaCl, halite. The Na^+ and Cl^- ions are arranged in a face-centered cubic lattice. (b) The same structure showing the edge-sharing octahedra about the Na^+. Similar edge-sharing octahedra could be drawn about Cl^-.



AX structure (CN = 6) – common minerals

- alkali halides with radius ratios up to RbCl
- alkaline earth oxides, including MgO (periclase)
- Some transition metal oxides, including FeO (Wüstite)



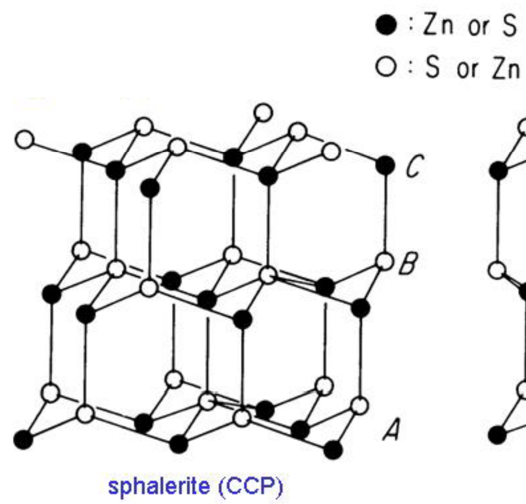
AX structure (CN = 4)

CN = 4: the wurtzite and sphalerite structures

- polymorphs of ZnS

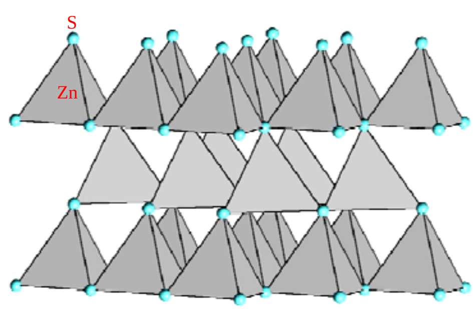
wurtzite

sphalerite

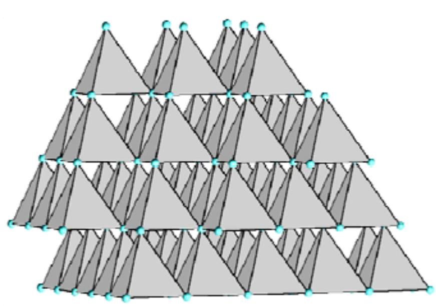


Both composed of a network of corner-linked tetrahedra that results from filling all the up-ward pointing tetrahedral sites between the anions

Wurtzite structure
Oblique view
Cation CN = 4

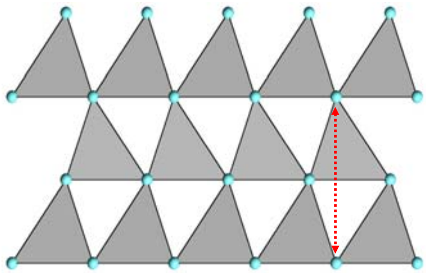


Sphalerite structure
Oblique view
Cation CN = 4

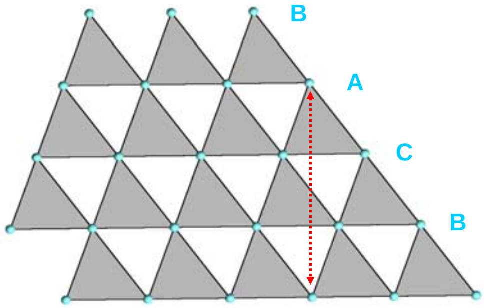


Differ in the packing of the anion (S^{2-})

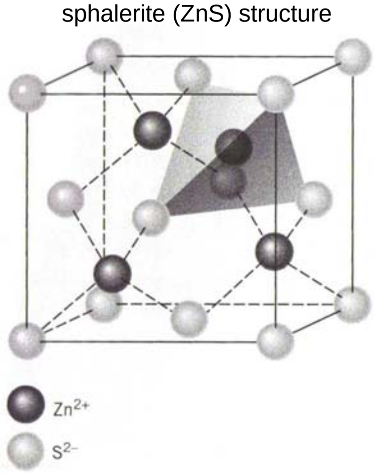
Wurtzite structure
Side view
HCP array of S



Sphalerite structure
Side view
CCP array of S



sphalerite (ZnS) structure



diamond structure

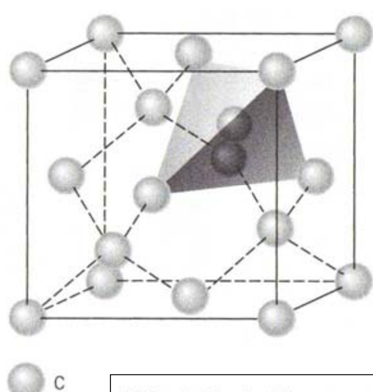


FIG. 4.19 (a) The structure of sphalerite, ZnS. Both Zn^{2+} and S^{2-} are in a face-centered cubic array. Zn^{2+} is in tetrahedral coordination with four S^{2-} neighbors (see also Fig. 4.10*c*). (b) The structure of diamond, C. The coordination of C by four nearest carbon neighbors is tetrahedral. (See also Fig. 3.18.)

Simple structures – AX_2

CN = 8: the fluorite structure

CN = 6: the rutile structure

AX_2 structure (CN = 8)

CN = 8: the fluorite structure

- anions in a simple cubic (SC) array
- cations fill one-half the cubic sites (cation CN = 8)
- anion CN = 4
- cation polyhedra (cubes) share edges

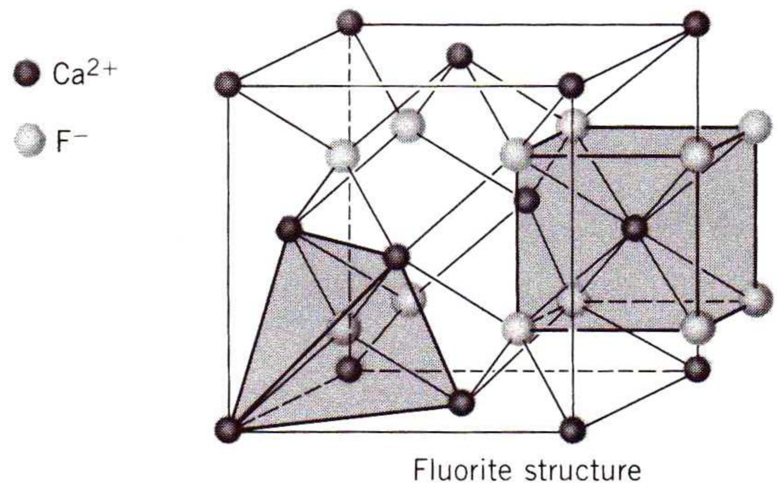
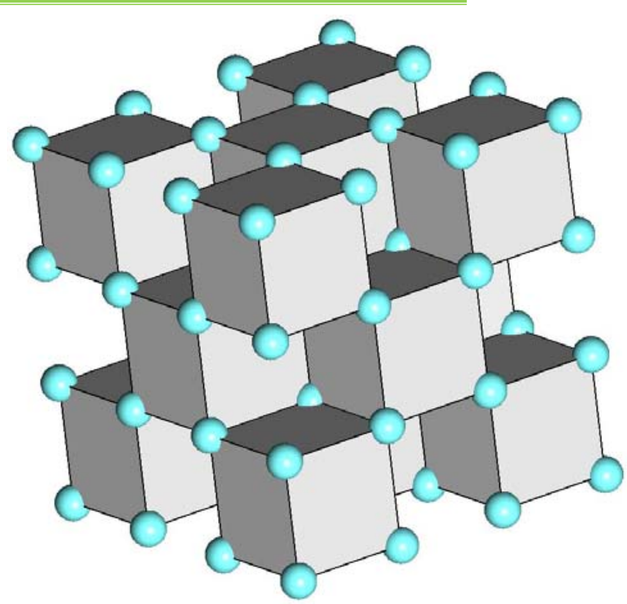


FIG. 4.20 The structure of fluorite, CaF_2. Ca^{2+} ions are arranged in a face-centered cubic lattice. The F^- ions are in simple cubic packing (SCP) with Ca^{2+} occupying the voids at the centers of *alternating* cubic interstices.

Polyhedral representation of the fluorite structure

Ca in FCC arrangement

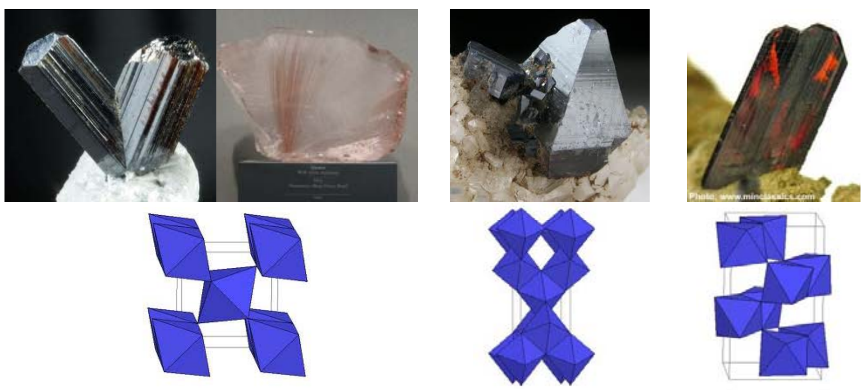
CN = 8



AX_2 structure (CN = 6)

CN = 6: The rutile structure

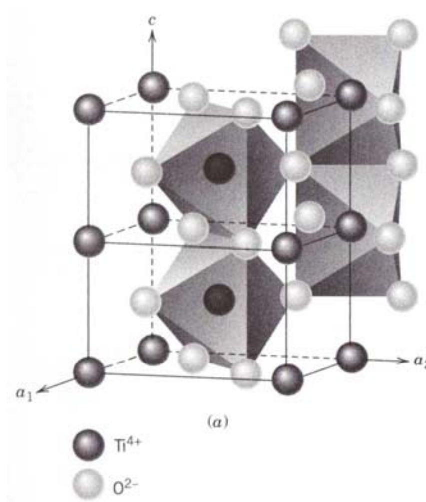
Polymorphes of TiO_2

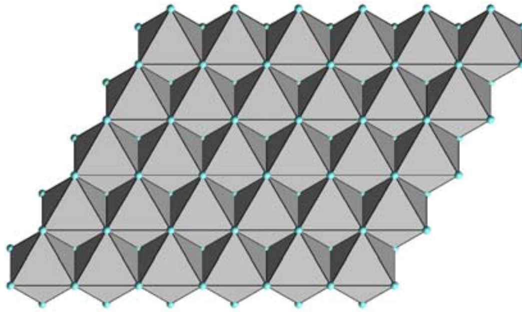


Rutile Anatase Brookite

AX_2 structure (CN = 6)

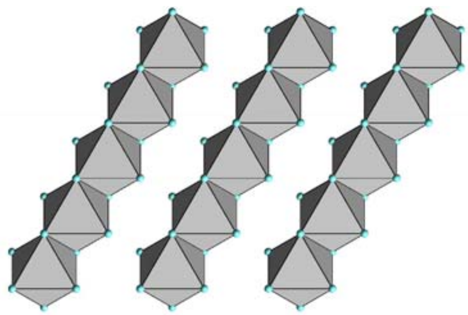
- anions are in an approximately HCP array
- cations occur as chains of edge-sharing octahedra
- chains are connected via corners
- chains are formed by filling one-half the octahedral sites in a HCP sheet





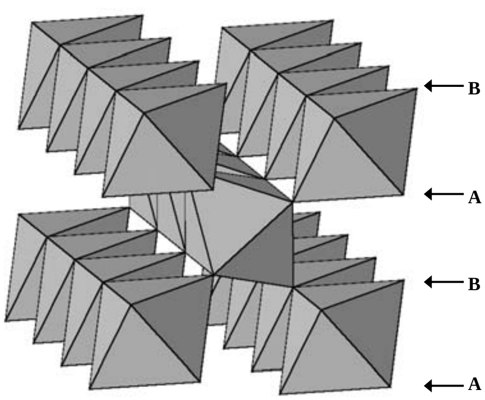
HCP array, all octahedral sites filled

→ sheet of edge-shared octahedra



HCP array, one-half of the octahedral sites occupied

→ chains of edge-shared octahedra



Rutile (TiO_2) structure:

Chains of edge-shared octahedra cross-linked by shared corners

Corresponds to filling one-half the octahedral voids in an HCP array.

Occupied sites alternate between layers.

Oxides and hydroxides

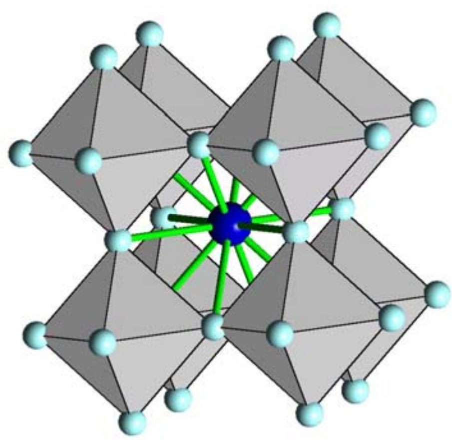
Perovskite structure (ABO_3)
Spinel structure (AB_2O_4)
Corundum group

Simple layered hydroxides

Oxyhydroxides

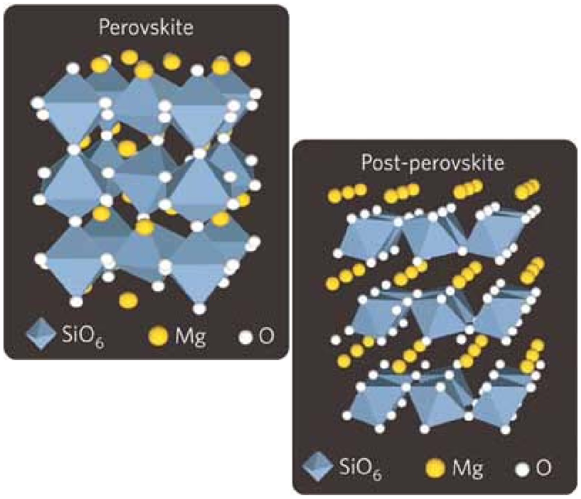
Perovskite structure (ABO_3)

- Named for the mineral perovskite: $CaTiO_3$
- A cations are large, CN = 12
- B cations have CN = 6, form a network of corner-linked octahedra
- This structure is adopted by a very large number of compounds



Perovskite structure (ABO_3)

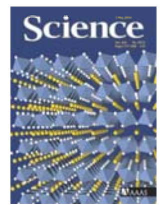
- Mg-silicate perovskite $MgSiO_3$ – primary mineral in the upper part of lower mantle



Post-Perovskite Phase Transition in $MgSiO_3$

Motohiko Murakami,[1*] Kei Hirose,[1*] Katsuyuki Kawamura,[1] Nagayoshi Sata,[2] Yasuo Ohishi[3]

In situ x-ray diffraction measurements of $MgSiO_3$ were performed at high pressure and temperature similar to the conditions at Earth's core-mantle boundary. Results demonstrate that $MgSiO_3$ perovskite transforms to a new high-pressure form with stacked SiO_6-octahedral sheet structure above 125 gigapascals and 2500 kelvin (2700-kilometer depth near the base of the mantle) with an increase in density of 1.0 to 1.2%. The origin of the D" seismic discontinuity may be attributed to this post-perovskite phase transition. The new phase may have large elastic anisotropy and develop preferred orientation with platy crystal shape in the shear flow that can cause strong seismic anisotropy below the D" discontinuity.



Murakami et al. (2004) Science, 304:855.

Spinel structure (AB_2O_4)

- The spinel-type oxides are very common accessory (minor) minerals in igneous, metamorphic, and sedimentary rocks
- Generally dark-colored and opaque
- based on a CCP array of oxygen
- cations occur in tetrahedral and octahedral coordination
- the ratio of tetrahedra : octahedra = 1:2

Spinel structure (AB_2O_4)

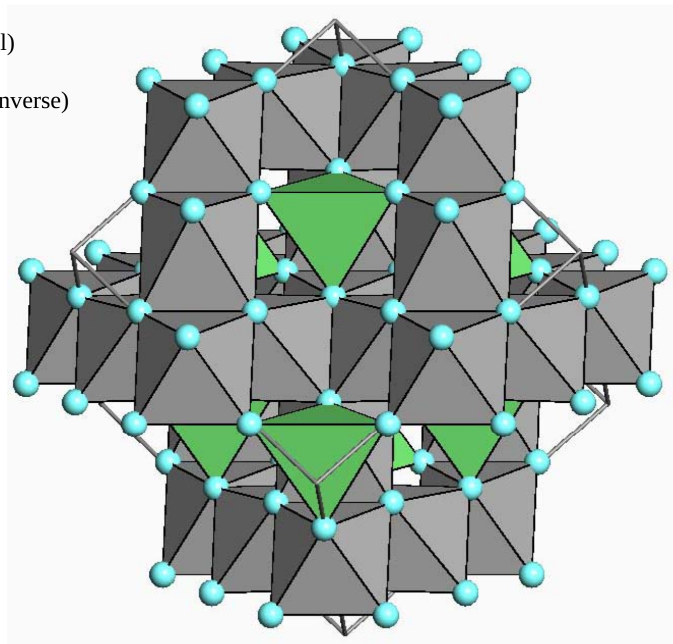
- Chemistry of spinels is complex (Klein p372-373)

  Spinels can be

  1. "normal": octahedral sites filled with "B" cations
  2. "inverse": "B" cations fill the tetrahedral sites, "A" and "B" cations on the octahedral sites

Spinel structure:
$A^{(4)}B^{(6)}{}_2O_4$ (normal)

$B^{(4)}$ $[B^{(6)}A^{(6)}]$ O_4 (inverse)



Spinel structure (AB_2O_4)

- Most spinels lie somewhere between these extremes

- Most also exhibit Mg/Fe solid solution

  Examples: chromite - magnesiochromite
  magnetite - magnesioferrite

Corundum structures

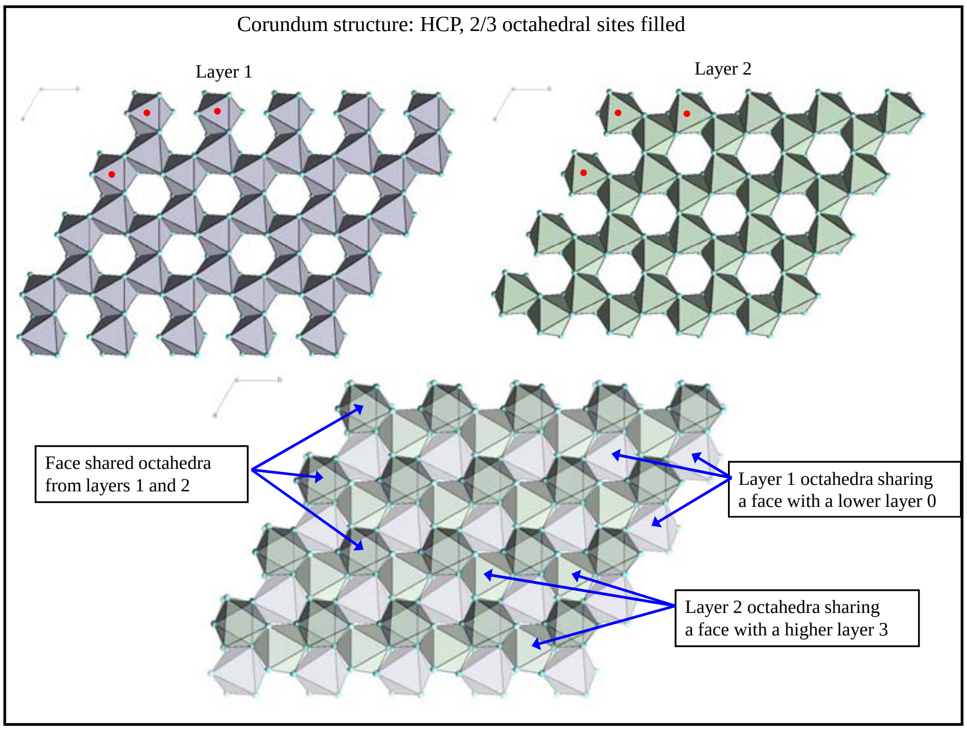
Minerals with the corundum structure include:

- corundum Al_2O_3; varieties include
  sapphire (blue), ruby (red)
- hematite Fe_2O_3
- ilmenite $FeTiO_3$

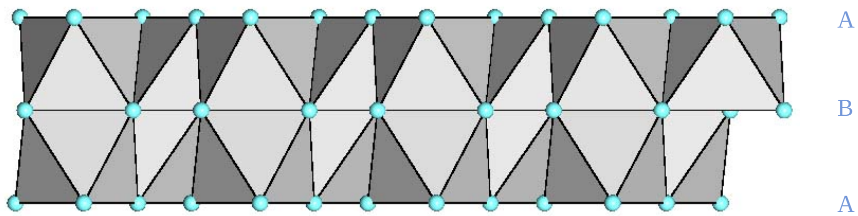



Corundum structures

- based on an HCP array of oxygen.
- all cation have CN=6
- cations fill 2/3 of the octahedral sites
- each octahedron shares a face with one other octahdron



Corundum structure, side view: HCP array of anions



Simple layered hydroxides

- Common minerals in soil environments and represent important structural components of more complex minerals such as the phyllosilicates (sheet silicates).

Simple layered hydroxides

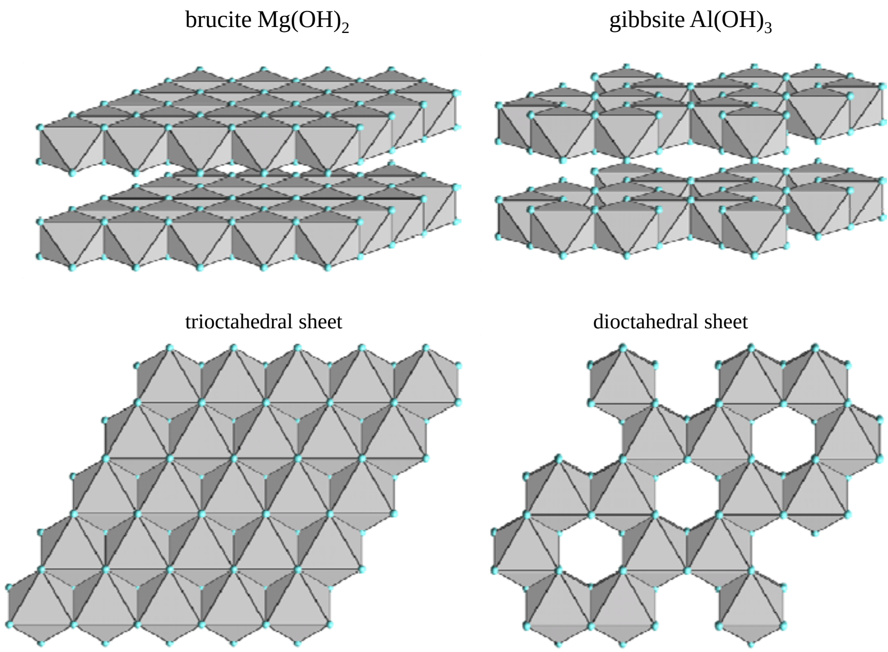
- Based on an HCP array of hydroxyl (OH^-) ions
- cations have CN=6
- Every other layer of octahedra filled
- Layers held together by weak Van der Waals and/or hydrogen bonding

Simple layered hydroxides

- Two main types depending on the charge of the cations

+2 cations fill all the octahedra in a sheet: “trioctahedral"
Example: brucite

+3 cations fill 2/3 of the octahedra in a sheet: "dioctahedral"
Example: gibbsite



Oxyhydroxides

- many are based on HCP anion arrays
- Typically, metal cations with CN = 6
- Examples: goethite FeO(OH) - a common soil and alteration mineral isostructural with diaspore AlO(OH) (a component of bauxite ores).

goethite FeOOH