Metal and Ceramic Crystal Structures

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Goals of this Unit

- To compare and contrast the structures of metal, ceramics and polymer materials
- Explain the three most important structures for metals
- Describe factors affecting crystal structure in ceramics
- Define polymorphism

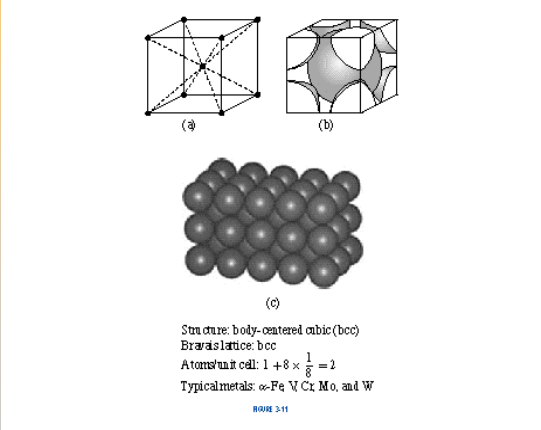
Metal structures

- Most elemental metals at room T are either:
  - Body Centered Cubic
    - not a close packed structure
  - Face Centered Cubic
    - also known as cubic close packed **(CCP)**
  - Hexagonal Close Packed **(HCP)**
- What is meant by "close packing"?

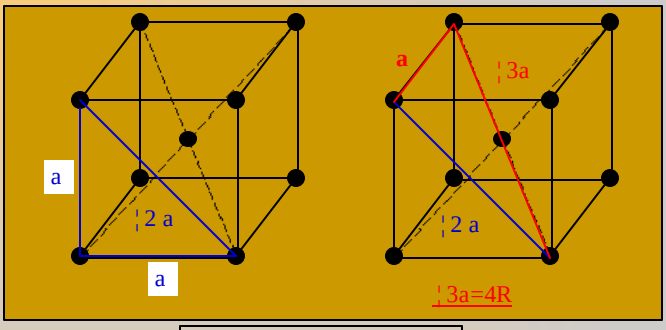
Cubic packing in metals

- Simple Cubic (**SC**)
  - One atom on each corner of the cell
  - Coordination number of 6
  - not a common metal structure
- Body-Centered Cubic (**BCC**)
  - One atom on each corner and one in the center of the cell volume
  - Coordination number of 8
- Face-Centered Cubic (**FCC** or **CCP**)
  - One atom on each corner and on each face
  - Coordination number of 12

BCC structure of metals



BCC metals

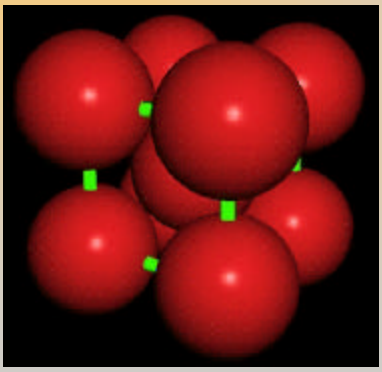


$$a = \frac{4R}{\sqrt{3}}$$

Cube length, a

Atomic Radius, R

BCC packing of metal atoms

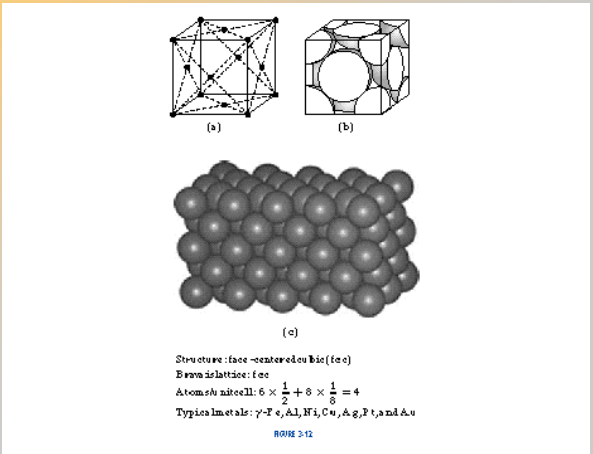


$$a = \frac{4R}{\sqrt{3}}$$

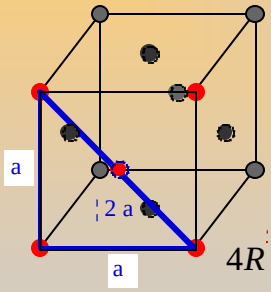
Cube length, a

Atomic Radius, R

FCC (or CCP) structure of metals



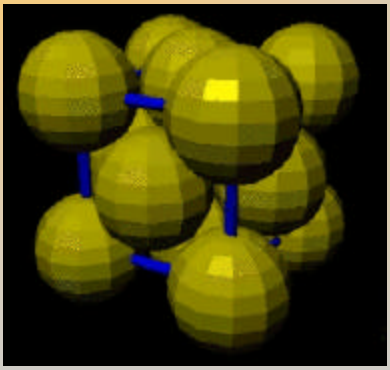
FCC (or CCP) in metals



$4R = a\sqrt{2}$

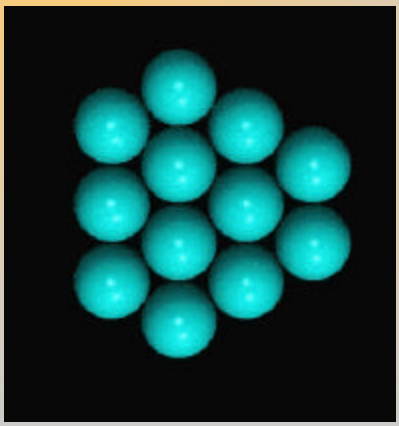
a = 2R-√2
Cube length, a
Atomic Radius, R

FCC (or CCP) 3-D example



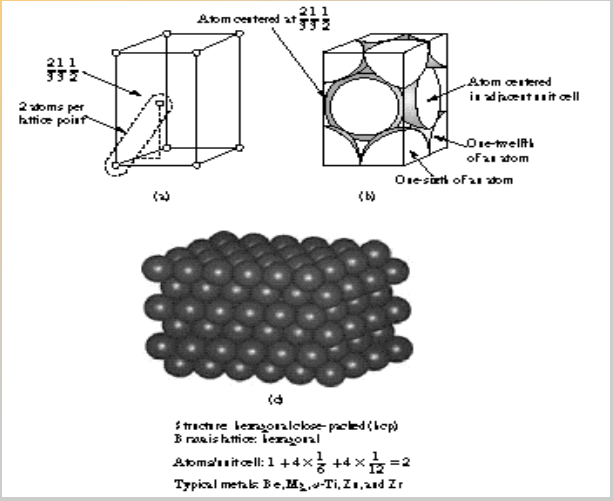
a = 2R-√2
Cube length, a
Atomic Radius, R

FCC Layer-Stacking

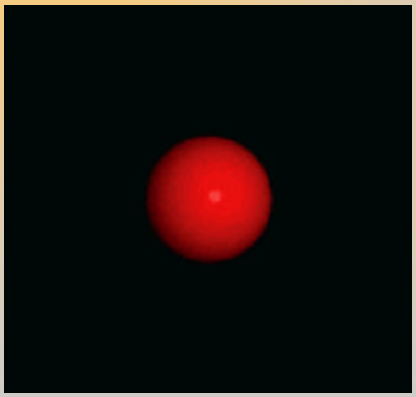


- The **CCP** structure has **a-b-c** stacking of close packed layers

HCP (Hexagonal Close-Packed) structure in metals

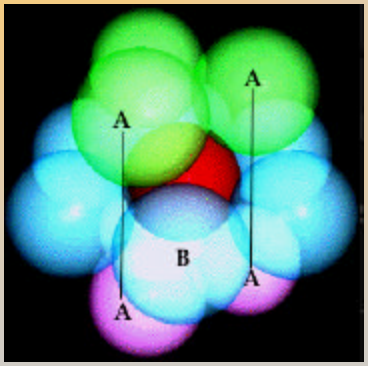


*Hexagonal Close Packed (**HCP**)*



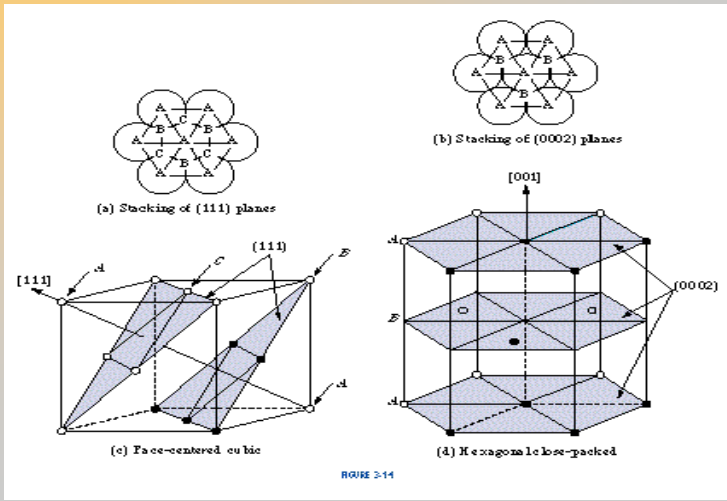
- Not all metals have cubic symmetry
- hcp is a common metal crystal structure
- "a-b-a" stacking of close packed layers

***HCP** Layer-Stacking*

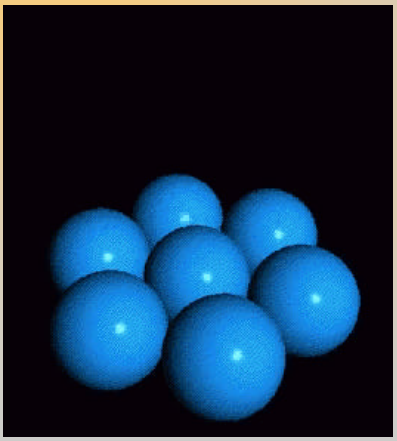


- Atoms in the first "layer" are directly below those in the third.
- **a-b-a-b-a-b-** etc.

*Stacking of cp planes in **CCP** and **HCP** metal structures*



CCP and HCP compared



HCP is shown above

- **CCP** is **abcabc...**
- **HCP** is **ababab...**

Structure of Selected Metals

Metal	Crystal Structure	Atomic Radius (nm)
Aluminum	FCC	0.1431
Chromium	HCP	0.1249
Cobalt	FCC	0.1253
Gold	FCC	0.1442
Copper	HCP	0.1278
Lead	FCC	0.1750

Example- Density of Cu

- If you know the crystal structure, the atomic radius and the atomic weight, you can calculate the density of a particular metal.
- Copper has an atomic radius 0.128 nm, a ccp crystal structure and an atomic weight of 63.5 g/mol. Calculate it's density.

Density of Cu

$$\text{density} = \frac{\text{mass}}{\text{volume}}$$

$$\rho = \frac{nA}{V_c N_A}$$

n = number of atoms/ unit cell
A = Atomic weight
V_c = volume per unit cell
N_A = Avogadro's number

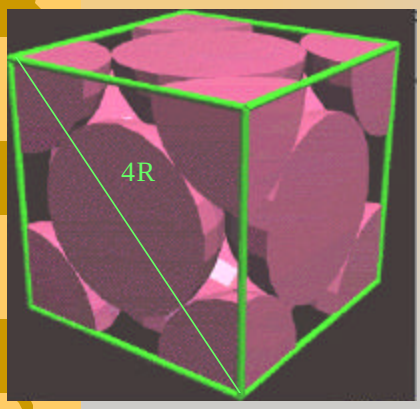
- number of atoms /unit cell = 4
- Atomic weight = 63.5 g/mol
- Unit cell volume = $16R^3$ 2
- Avogadro's number = 6.02×10^{23} atoms/mol
- **r = 8.89 g/cm^3** -measured value = 8.94 g/cm^3

Atomic Packing Factor

- Fraction of solid sphere volume in a unit cell
- e.g. for ccp
  - how many atoms are in the unit cell?
  - what is the cell volume?

$$\text{APF} = \frac{\text{volume of atoms in unit cell}}{\text{total cell volume}}$$

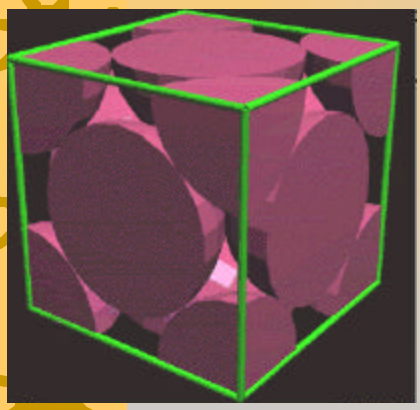
*Atomic Packing Factor for **CCP***



- There are 4 atoms in the cell - the volume of the atoms:

$$4 * \frac{4}{3}\pi R^3 = \frac{16}{3}\pi R^3$$

*Atomic Packing Factor for **CCP***



- What is the volume of the cube?
  - a^3 (length of side cubed)
- What is the volume in terms of R? (sphere radius)
  - a = 2R 2
  - (2R 2)^3 = 16R^3 2

*Atomic Packing Factor for **CCP***

$$APF = \frac{\text{volume of atoms in unit cell}}{\text{total cell volume}}$$

$$\frac{\frac{16}{3}\pi R^3}{16R^3\sqrt{2}} = \frac{\pi}{3\sqrt{2}}$$

$$= 0.74$$

The atomic packing factor for ccp is 0.74
(74% of the space is occupied by atoms)

Ceramic Crystal Structures

- Broader range of chemical composition than metals with more complicated structures
- Usually compounds between metallic ions (e.g. Fe, Ni, Al) - called cations - and non-metallic ions (e.g. O, N, Cl) - called anions
- Bonding will usually have some covalent character but is usually mostly ionic

How do Cations and Anions arrange themselves in space???

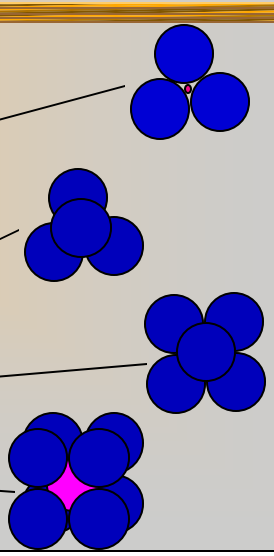
- Structure is determined by two characteristics:
  - Electrical charge
    - Crystal (unit cell) must remain electrically neutral
    - Sum of cation and anion charges in cell is 0
  - Relative size of the ions

Ceramic Crystal Structure

- The ratio of ionic radii (r_{cation}/r_{anion}) dictates the coordination number of anions around each cation.
- As the ratio gets larger (i.e. as $r_{cation}/r_{anion} \rightarrow 1$) the coordination number gets larger and larger.

Geometries of Ceramic Crystals

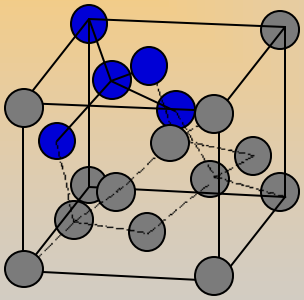
CN		
3	0.155 - 0.225	Triangular
4	0.255 - 0.414	Tetrahedron
6	0.414-0.732	Octahedron
8	0.732 - 1	Cube Center



Some common ceramic structures

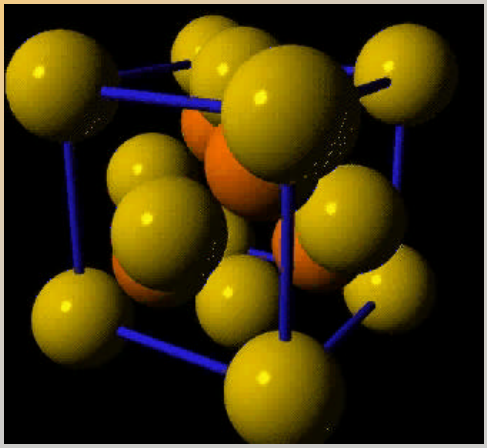
- Diamond
- Zincblende (sphalerite)
- Rock salt
- Cesium Chloride
- Fluorite
- Corundum
- Perovskite
- Spinel
- Silicates (complex)

Diamond Cubic Structure

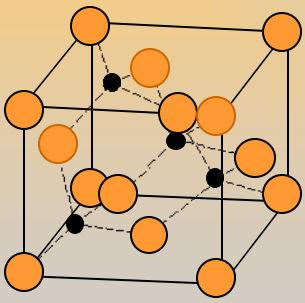


- All atoms are C
- 4 interior C atoms (tetrahedrally coordinated with corner and face-centered C atoms)

Diamond Cubic Structure



Zincblende Structure



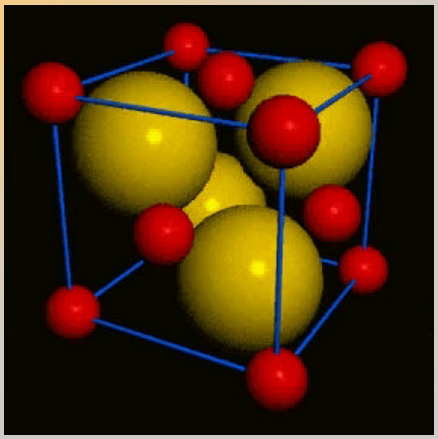
Coordination = 4

S

Zn

radius ratio = 0.402

Zincblende Structure



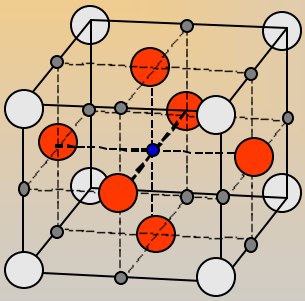
Zincblende Structure

- You could also draw this structure with a Zn atom at each corner and centered in each face with four S atoms inside the cell at alternate 1/4,1/4, 1/4 positions
- How many formula units are there per unit cell in the zincblende structure? In the diamond structure?

Zincblende- Bravais Lattice

- A 1/2,1/2,0 translation from any atom brings you to an identical atom
- Therefore, this is a **FCC** Bravais lattice (with one Zn and one S atom per lattice site)
- Note: diamond is also **FCC** (but neither is close packed like a **CCP FCC** metal)
- Many important compound semiconductors have the zincblende structure (e.g., GaAs)

Rock Salt Structure (NaCl)



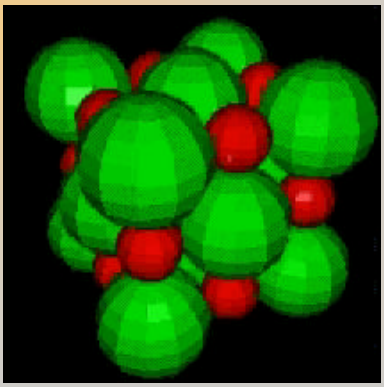
Coordination = 6

Cl

Na

radius ratio = 0.564

Rock Salt Structure



Rock Salt Structure

- Could also draw with Na at corners
- What is Bravais lattice for rock salt structure?
- How many formula units are there per unit cell in the rock salt structure
- MgO, FeO, NiO, CaO also have rock salt structure

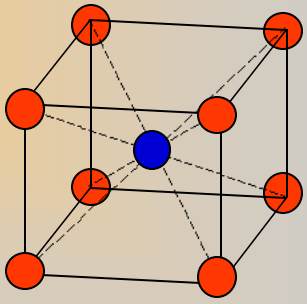
Cesium Chloride Structure (CsCl)

Coordination = 8

Cl

Cs

radius ratio = 0.939



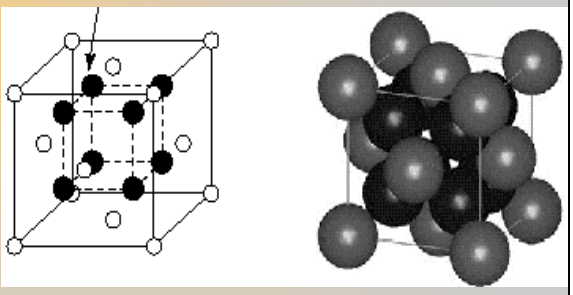
Cesium Chloride Structure

- Could also draw with Cs at each corner and Cl in body-center position
- What is Bravais lattice for CsCl structure?
- How many atoms are associated with each lattice point in the CsCl structure?
- How many formula units are there in a CsCl unit cell?

Flourite Structure (CaF_2)

F^- [at corners (¼ ¼ ¼)] ●

Ca^{2+} ○



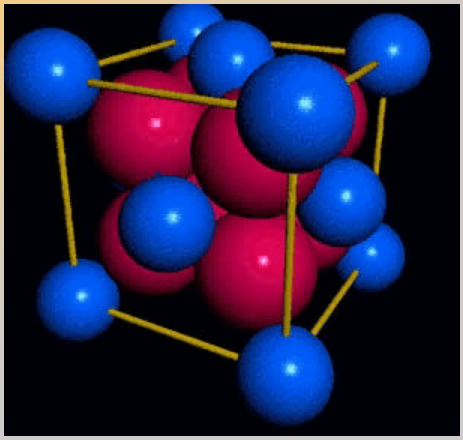
Structure: Flourite

Bravais Lattice: FCC

Ion/ Unit Cell: $4Ca^{2+} + 8F^- = 12$

Typical Ceramics: UO_2, ThO_2, and TeO_2

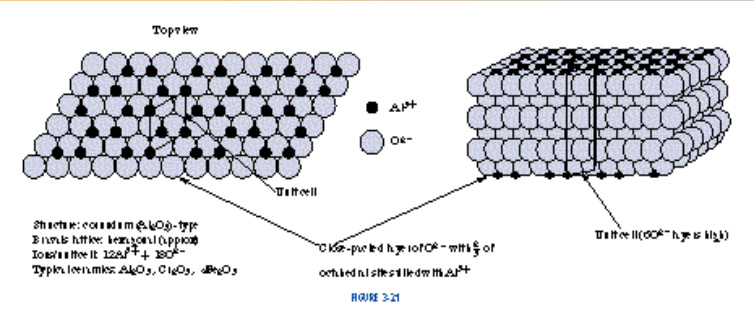
Fluorite Structure



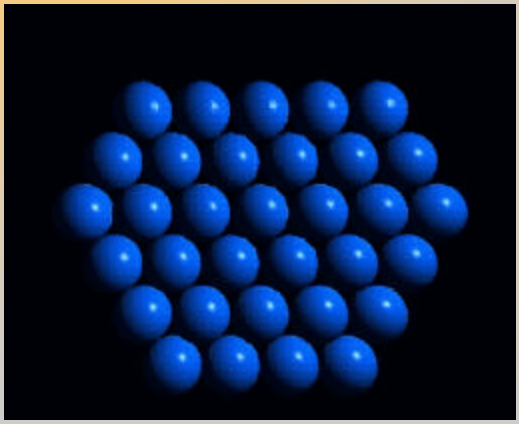
Flourite Structure

- How many formula units per unit cell of the flourite structure?
- How would you draw this cell with F at the corners of the cubic unit cell?

Corundum Structure (Al_2O_3)



Corundum Structure



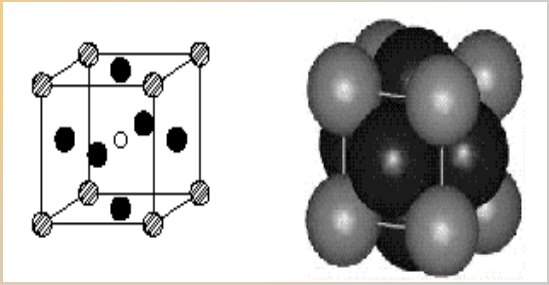
- Other materials that have the corundum structure are Fe_2O_3 and Cr_2O_3

Perovskite Structure ($BaTiO_3$)

Ti^{4+} at body center

Ca^{2+} at corners

O^{2-} at face centers



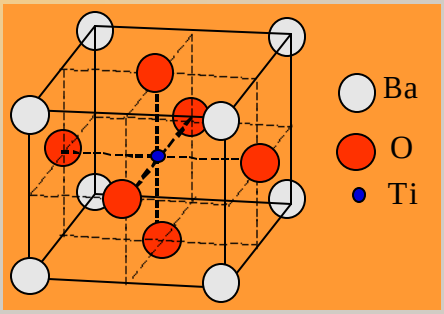
Structure: Perovskite

Bravais Lattice: Simple Cubic

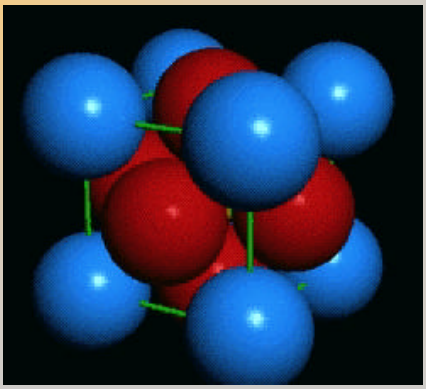
Ions/ Unit Cell: $1Ca^{2+} + 1Ti^{4+} + 3O^{2-} = 5$

Typical Ceramics: $CaTiO_3$, $BaTiO_3$

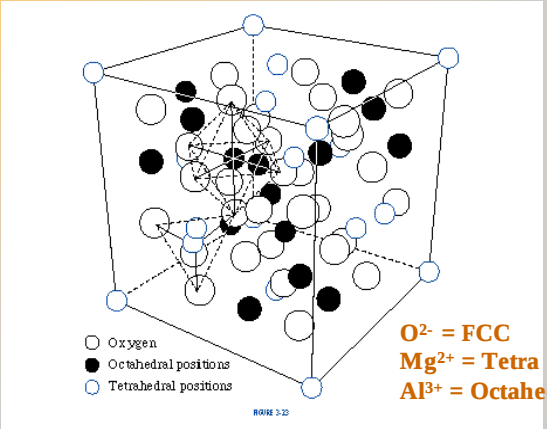
Perovskite Structure



Perovskite Structure



Spinel Structure ($MgAl_2O_4$)



O^{2-} = FCC
Mg^{2+} = Tetra
Al^{3+} = Octahedra

Spinel Structure

- The spinel structure is capable of wide variations in composition by substitution of various cations in both the tetrahedral and octahedral sites within the basic close packing of the oxygen anions
- Certain kinds of ceramic magnets (ferrites) and many refractory compounds have this structure

An alternative way to look at simple ceramic structures

- The anions form an "almost-close-packed" array (either "**ccp**" or "**hcp**") and the smaller cations occupy interstitial spaces within these "almost cp" arrays
- Any close packed array of N atoms contains N octahedral interstitial sites and (2N) tetrahedral sites
  - octahedral sites are larger than tetrahedral sites

Examples:

- Rock salt structure
  - anions form a "**ccp**" array with cations located in all of the octahedral sites
- Corundum structure (not discussed)
  - anions form a "**hcp**" array with cation located in 2/3 of the octahedral sites (maximum separation)

More examples

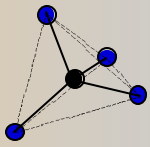
- Spinel structure
  - anions in "**ccp**" array with one kind of cations in 1/2 the octahedral sites and another kind of cations in 1/8 of the tetrahedral sites
- Zincblende structure
  - anions in "**ccp**" array with cations in 1/2 of the tetrahedral sites

Variations on the theme

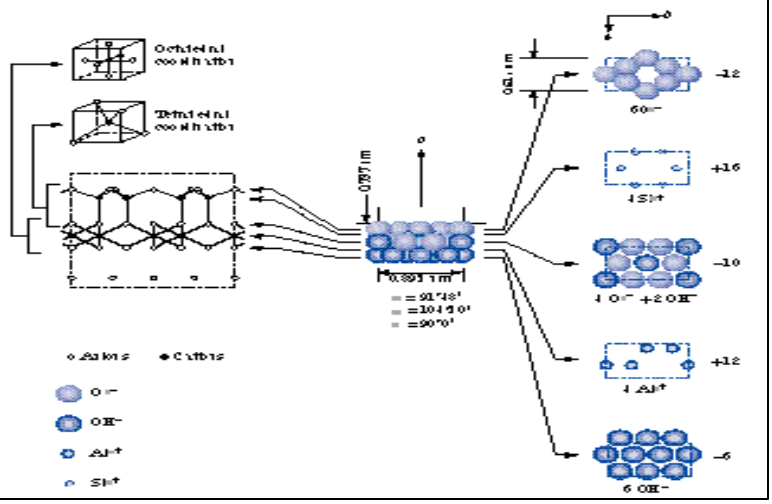
- Flourite structure
  - anions in simple cubic array with cations in 1/2 of the "cubic" (8-fold) interstitial sites
- CsCl structure
  - anions in simple cubic array with cations in every "cubic" site

Silicates

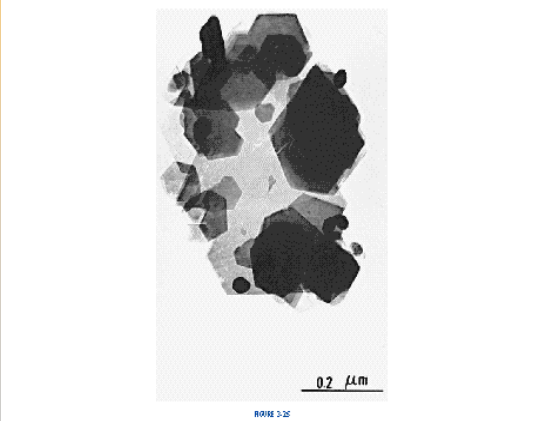
- Mineral compounds based on SiO_4^{4-} tetrahedra
- Linked together sharing corners, edges or faces
- Layered silicates
  - two dimensional sheet
  - cations between sheets
  - clays - kaolinite (has adjacent $Al_2(OH)_4^{4+}$)
    - bonding within layers is strong
    - bonding between layers is weak



Kaolinite structure
$Al_2(OH)_4Si_2O_5$



Electron micrograph of kaolinite particles (from a kaolin)



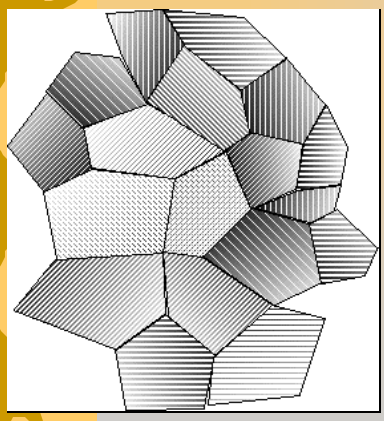
Crystalline & Noncrystalline Materials

- Single crystals
  - Repeated arrangement of atoms extends throughout the entire specimen
  - All unit cells have the same orientation
  - Exist in nature, but rarely (e.g. gem stones)
  - Can also be synthetically grown (e.g., Si)
    - Without external constraints, will often have flat, regular faces

Polycrystalline Materials

- Most crystalline materials are composed of many small crystals called **grains**
- Crystallographic directions of adjacent grains are usually random
- There is usually atomic mismatch where two grains meet - this is called a **grain boundary**
- Most powdered materials have many randomly oriented grains which sinter to form polycrystalline specimens

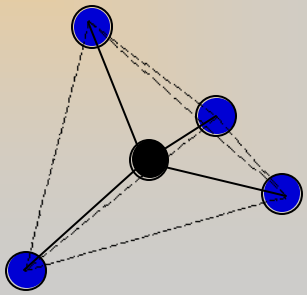
Schematic of Polycrystalline Material



- Crystals of different
  - sizes
  - orientations
  - shapes
- Grain Boundaries
  - mismatch between two neighboring crystals
- Different phases
  - interphase boundaries

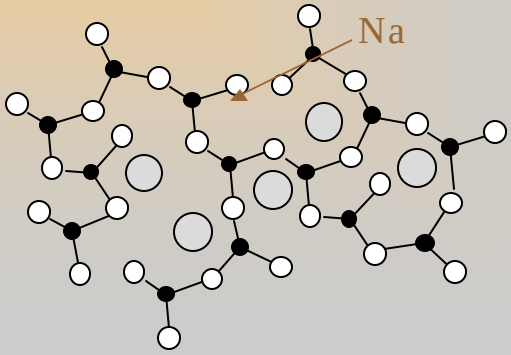
Glass Structure

- The basic structural unit of a silicate glass is the SiO_4 tetrahedron
- Link together sharing corners to form a 3-D network



Glasses

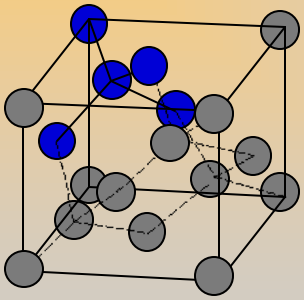
- Beyond the short range order the structure is random
- Other ions may also be present



Polymorphism and Allotropy

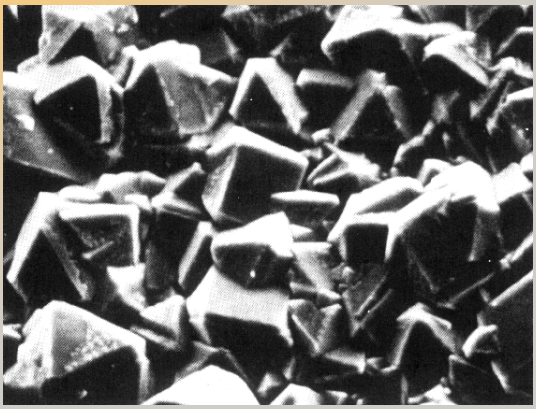
- Some materials may have more than one crystal structure depending on temperature and pressure - called POLYMORPHISM
- Carbon (diamond, graphite, fullerenes)
- Silica (quartz, tridymite, cristobalite, etc.)
- Iron (ferrite, austenite)

Diamond

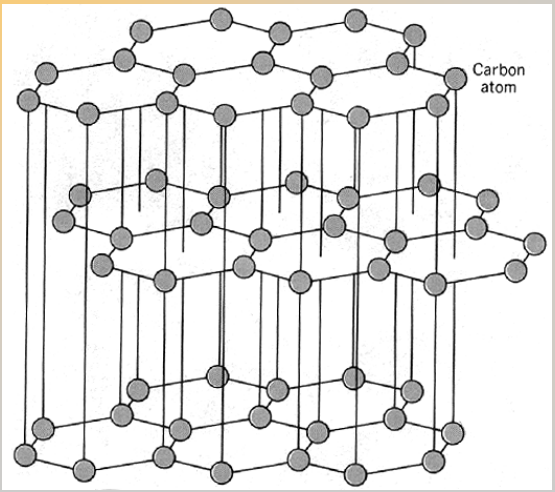


- Covalent bonds
  - *extremely* strong
- HARD
- Low electrical conductivity
- Optically transparent

Diamond Thin Film

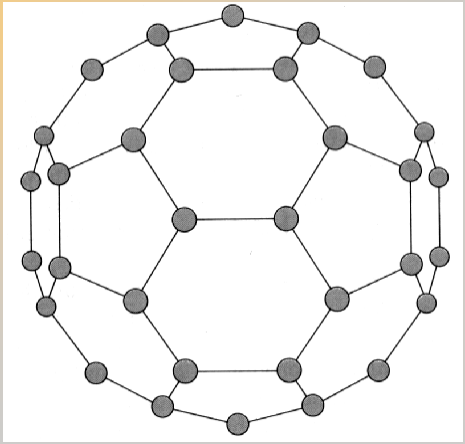


Carbon - Graphite



not hcp

Fullerenes



Polymer Structures

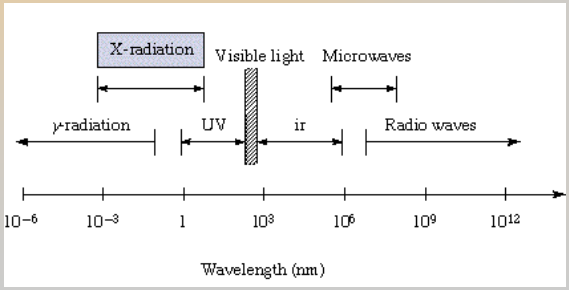
- Chainlike structures of long polymeric molecules (usually involving C, H, and O + other elements)
- Usually mostly noncrystalline
  - Extremely complex and elongated molecules do not readily "line up" on cooling to crystallize
- Structure is very dependent on thermal history (so are properties)

Semiconductor Structures

- Technologically, single crystals are very important
- More "perfect" than any other class of materials (purer, fewer dislocations)
- Elemental semiconductors (Si and Ge) are of the diamond cubic structure
- Compound semiconductors (GaAs, CdS) have zincblende (similar to diamond cubic)

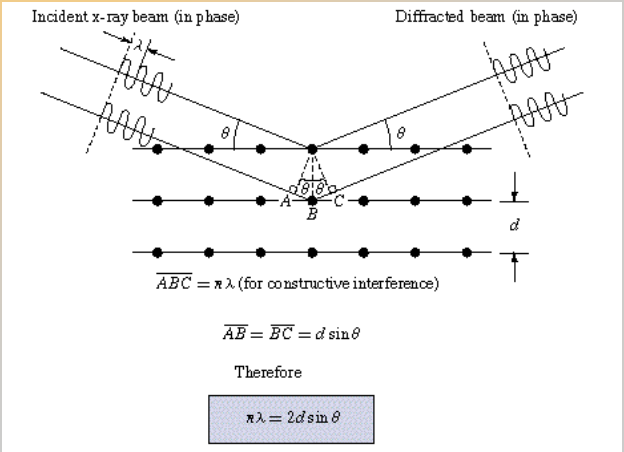
How are crystal structures determined?

- X-ray diffraction
  - Interplanar distances in crystals are of same length as x-rays, so groups of planes can cause diffraction

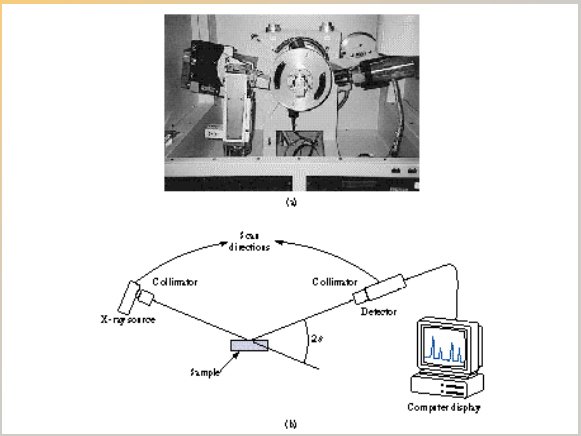


Diffraction occurs only at certain angles by constructive interference

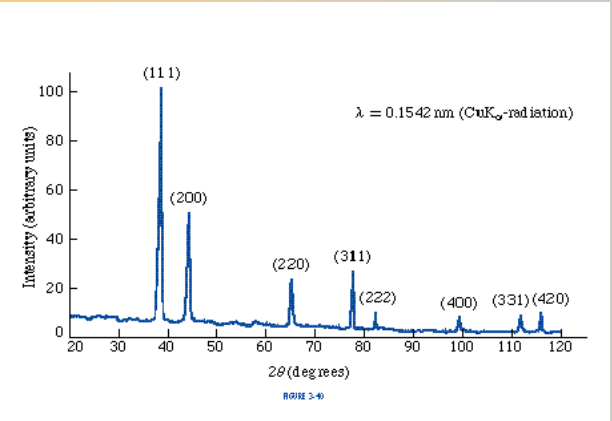
- Bragg's law



Diffractometer setup



Diffractometer pattern for an fcc structure



Review

- Metal structures are usually fcc (ccp), bcc or hcp
- Ceramics have more complex structures dictated by the electrical charge and relative size of the atoms/ions involved
- Solids can be single crystal, polycrystalline, or amorphous
- A solid can have various forms **(polymorphism)**
- X-ray diffraction is used to determine crystal structures

End of Lecture, Unit 1–3

- READ
  - Class Notes & Callister 2000, pp. 30-59, 382-40
  - Shackelford 2000, pp. 64-88
- Polymer (Macromolecular) structure
  - Next Unit 1–4