

# MEAM/MSE 507

# Fundamentals of Materials

Prof. Jordan R. Raney

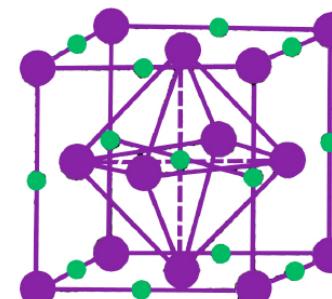
**Week 5, Lecture 2: Physical crystals (part 2)**  
**Asynchronous**

# Interstitial sites

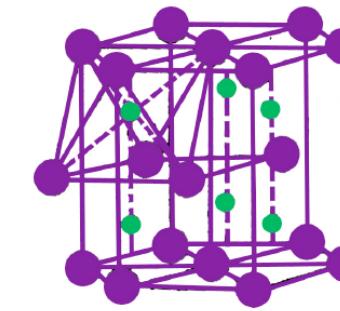
- The different lattices have different locations of “interstitial” gaps
- Important for diffusion, plasticity, etc., and for determining crystal structure in ionic solids

**Octahedral Sites** (surrounded by six atoms to form octahedron)

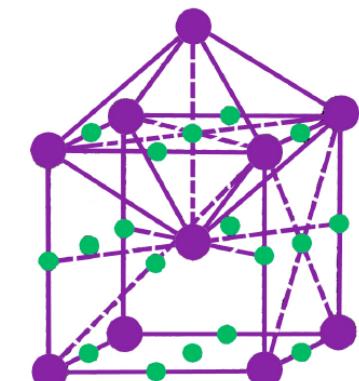
O sites



FCC



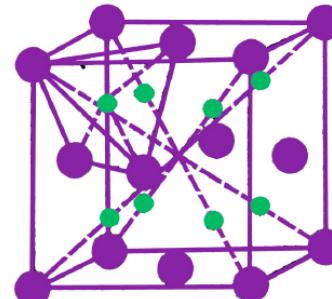
HCP



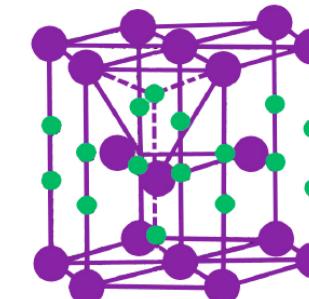
BCC

**Tetrahedral Sites** (surrounded by four atoms to form tetrahedron)

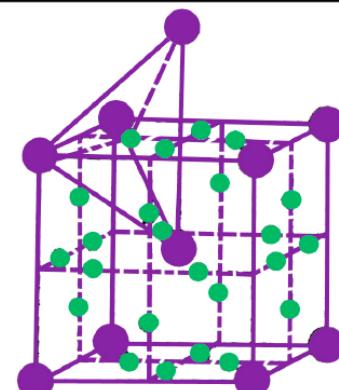
T sites



FCC



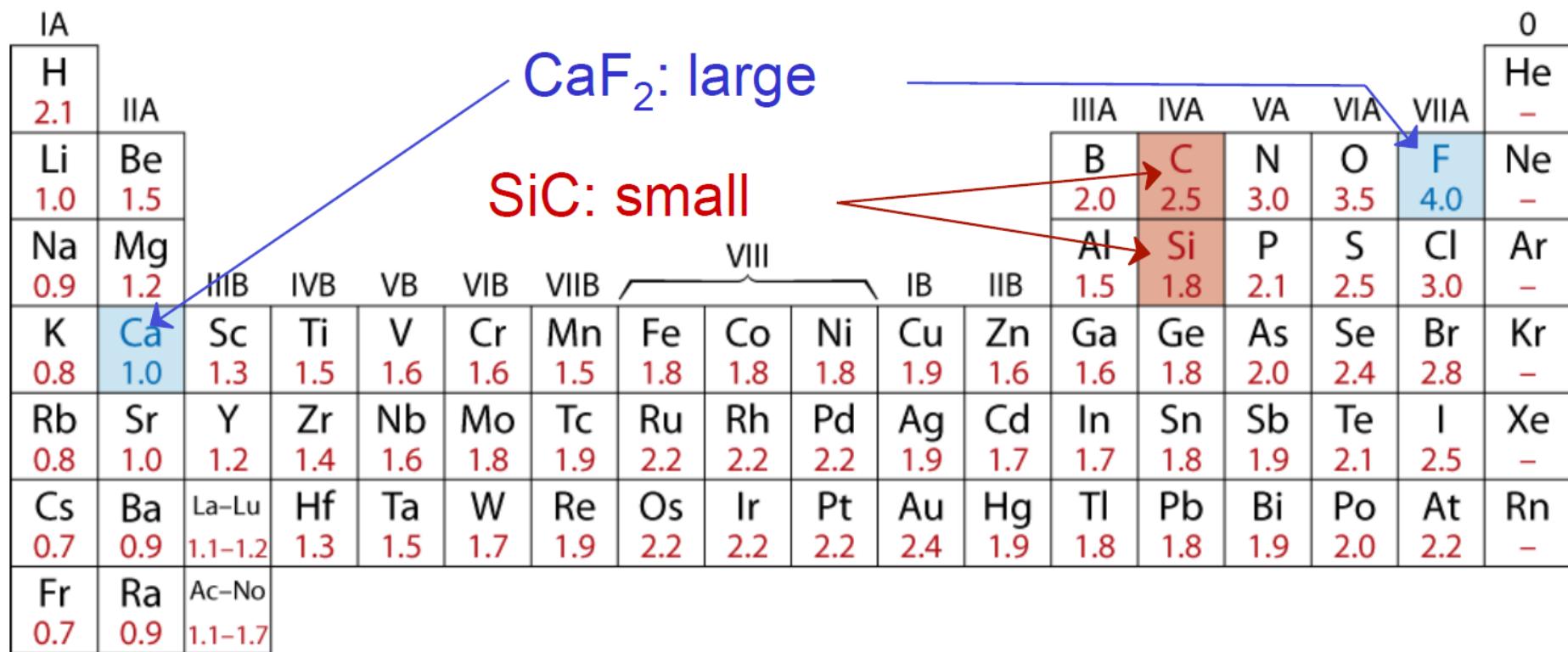
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BCC

# Ceramics

- Can be ionic and/or covalent in character
  - similar EN
  - large differences in EN

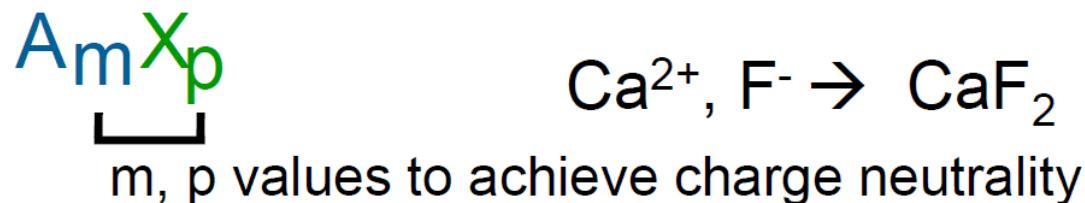


# Ceramic crystal structures

## Oxide structures

### 1. Charge neutrality

- Net charge should be zero - reflected in chemical unit

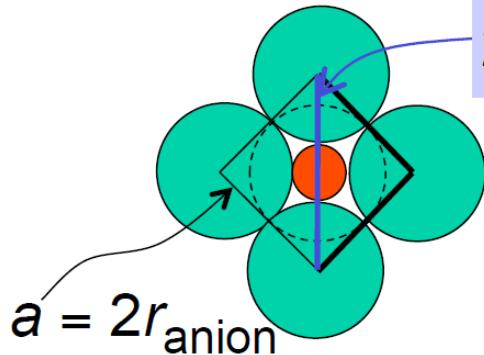


### 2. Ion size

- oxygen anions (-), typically larger than metal cations (+)
- close packed oxygen in a lattice (often FCC)
- cations fit into interstitial sites/holes in the oxygen ion lattice
- holes in FCC anion lattice
  - octahedral hole (6 coordinated)
  - tetrahedral hole (4 coordinated)

# Cation-anion radius ratio

- Determine  $r_{\text{cation}}/r_{\text{anion}}$  so that it just fits



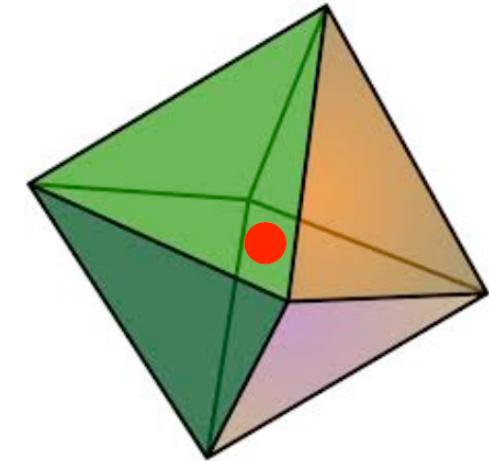
$$2r_{\text{anion}} + 2r_{\text{cation}} = \sqrt{2}a$$

$$2r_{\text{anion}} + 2r_{\text{cation}} = 2\sqrt{2}r_{\text{anion}}$$

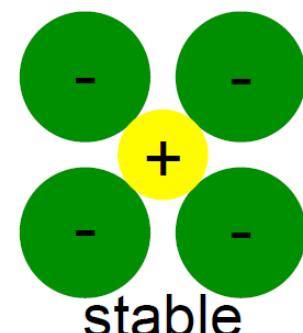
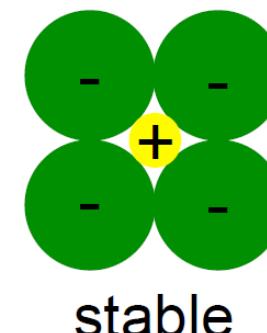
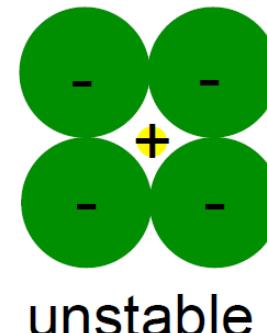
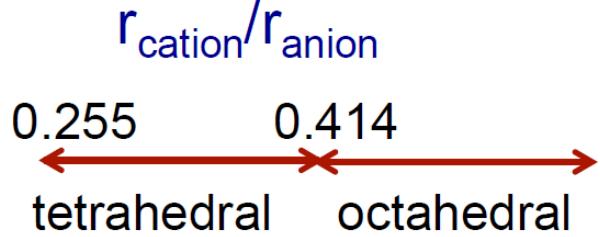
$$r_{\text{anion}} + r_{\text{cation}} = \sqrt{2}r_{\text{anion}}$$

$$r_{\text{cation}} = (\sqrt{2} - 1)r_{\text{anion}}$$

$$\frac{r_{\text{cation}}}{r_{\text{anion}}} = \sqrt{2} - 1 = 0.414$$



For a stable cation/anion configuration, ions should be in contact, but with minimum distortion of the lattice →

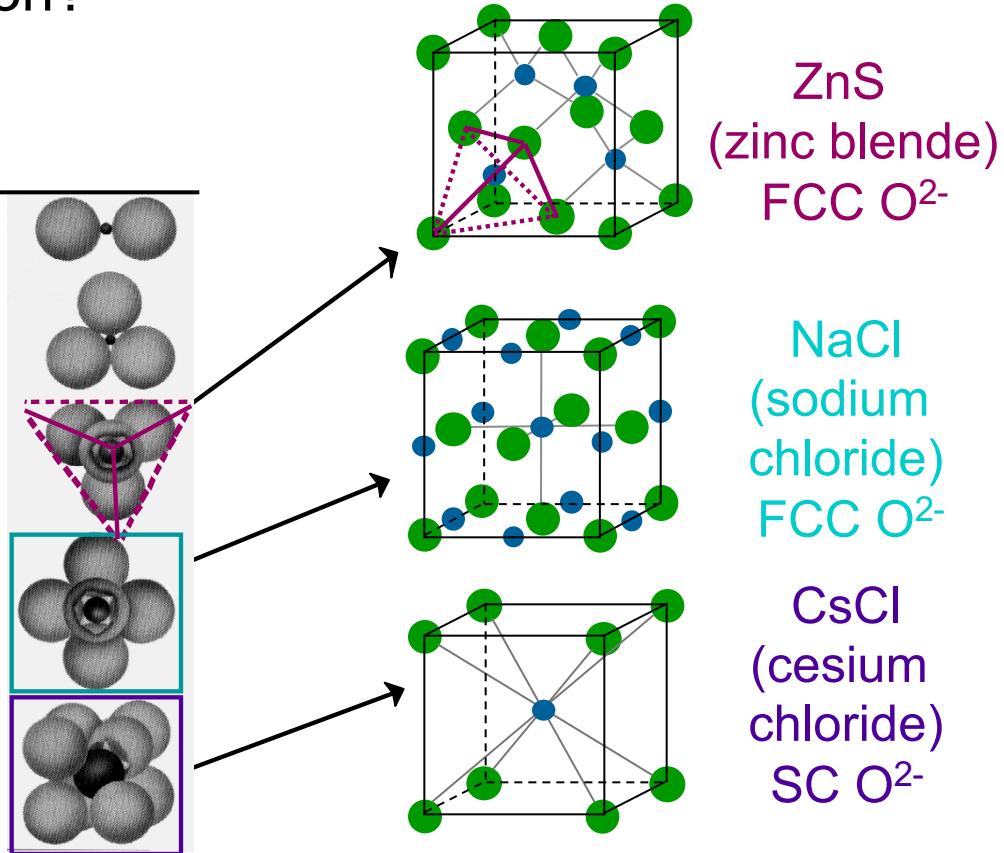


# Coordination number and ionic radii

- Coordination Number increases with  $\frac{r_{\text{cation}}}{r_{\text{anion}}}$

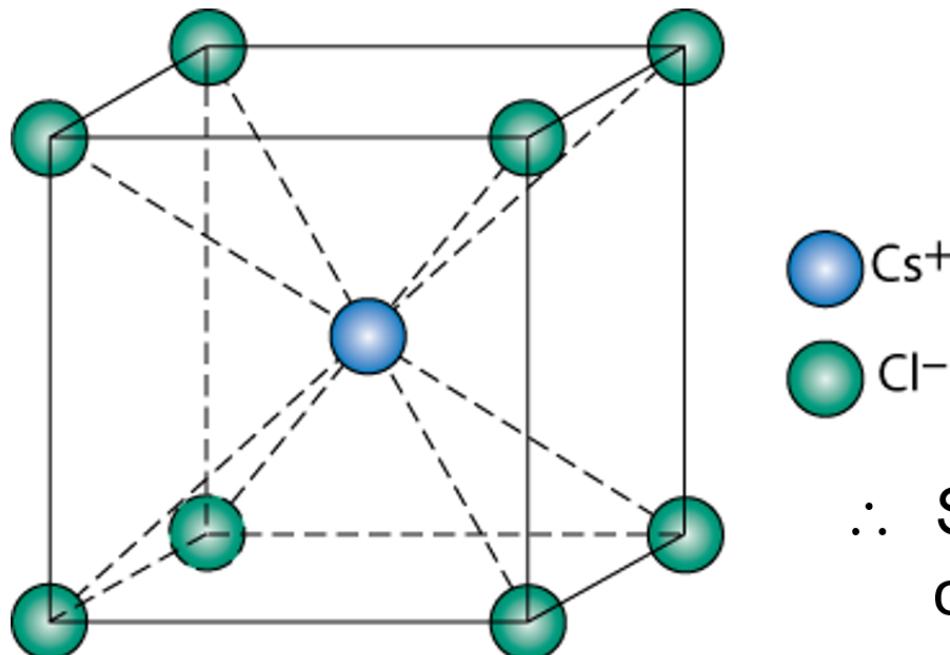
To form a stable structure, how many anions can fit around a cation?

$\frac{r_{\text{cation}}}{r_{\text{anion}}}$	Coord. Number	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic



# Examples

Cesium Chloride structure:



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

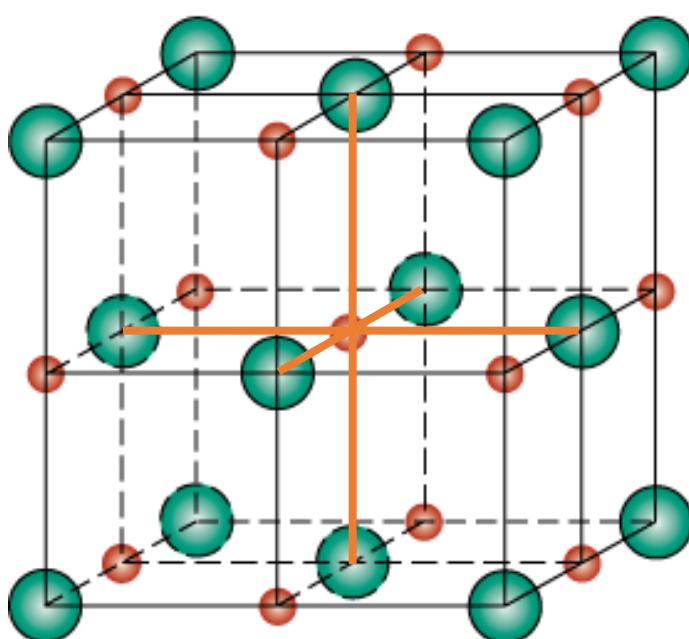
∴ Since  $0.732 < 0.939 < 1.0$ ,  
cubic sites preferred

So each Cs<sup>+</sup> has 8 neighbor Cl<sup>-</sup>

# Rock salt structure

Same concepts can be applied to ionic solids in general.

Example: NaCl (rock salt) structure



●  $\text{Na}^+$   $r_{\text{Na}} = 0.102 \text{ nm}$

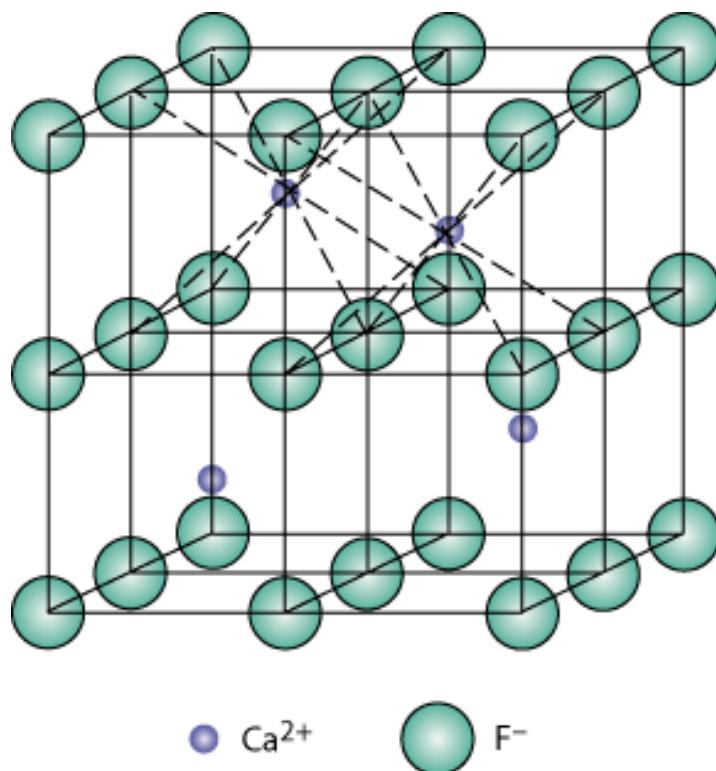
●  $\text{Cl}^-$   $r_{\text{Cl}} = 0.181 \text{ nm}$

$$r_{\text{Na}}/r_{\text{Cl}} = 0.564$$

∴ cations ( $\text{Na}^+$ ) prefer octahedral sites

# AX<sub>2</sub> crystal structures

## Fluorite structure unit cell

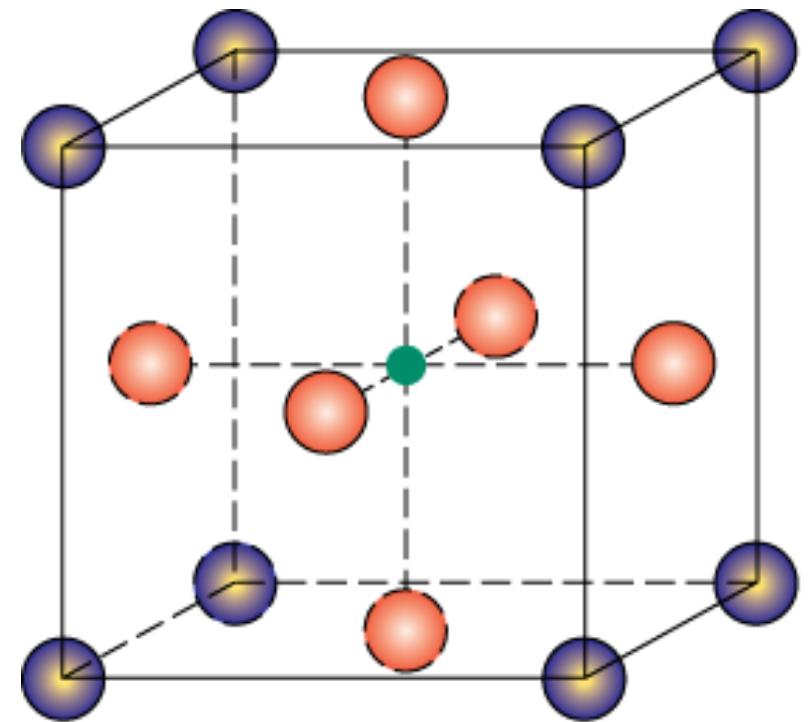
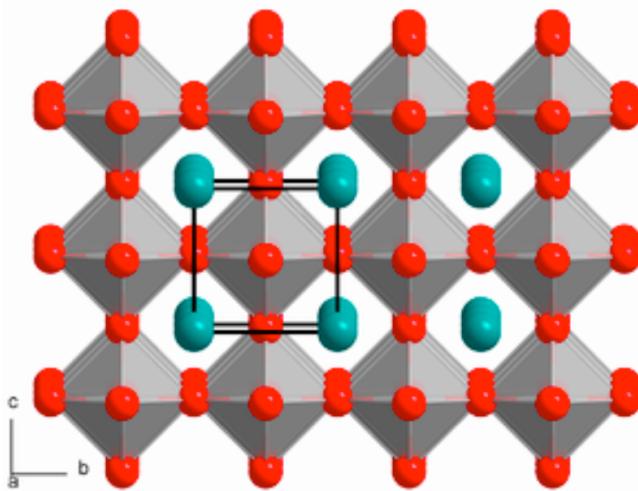


- Calcium Fluorite (CaF<sub>2</sub>)
- Cations in cubic sites
- UO<sub>2</sub>, ThO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>
- Antifluorite structure – positions of cations and anions reversed

# ABX<sub>3</sub> crystal structures

- Perovskite structure

Ex: complex oxide



# Hybridization

Bond Hybridization is possible when there is significant covalent bonding

- hybrid electron orbitals form
- For example for SiC
  - $X_{\text{Si}} = 1.8$  and  $X_{\text{C}} = 2.5$

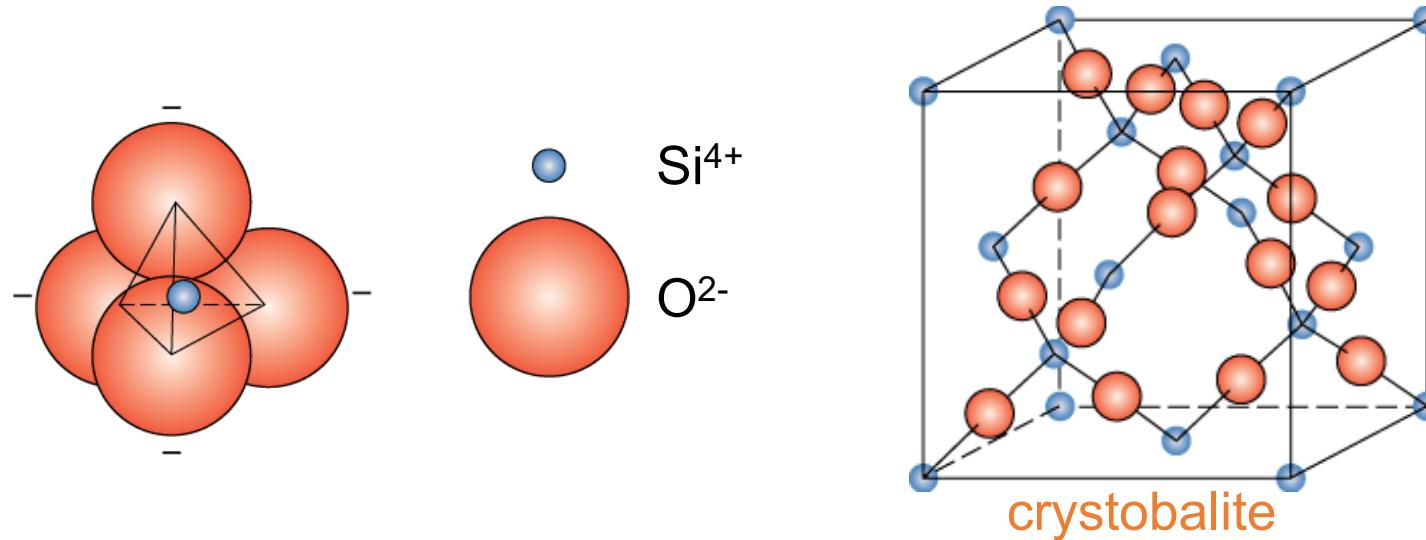
$$\% \text{ ionic character} = 100 \left\{ 1 - \exp \left[ -(X_{\text{Si}} - X_{\text{C}})^2 / 4 \right] \right\} = 11.5\%$$



- ~ 89% covalent bonding
- Both Si and C prefer  $sp^3$  hybridization
- Both Si and C atoms occupy tetrahedral sites

# Silicate ceramics

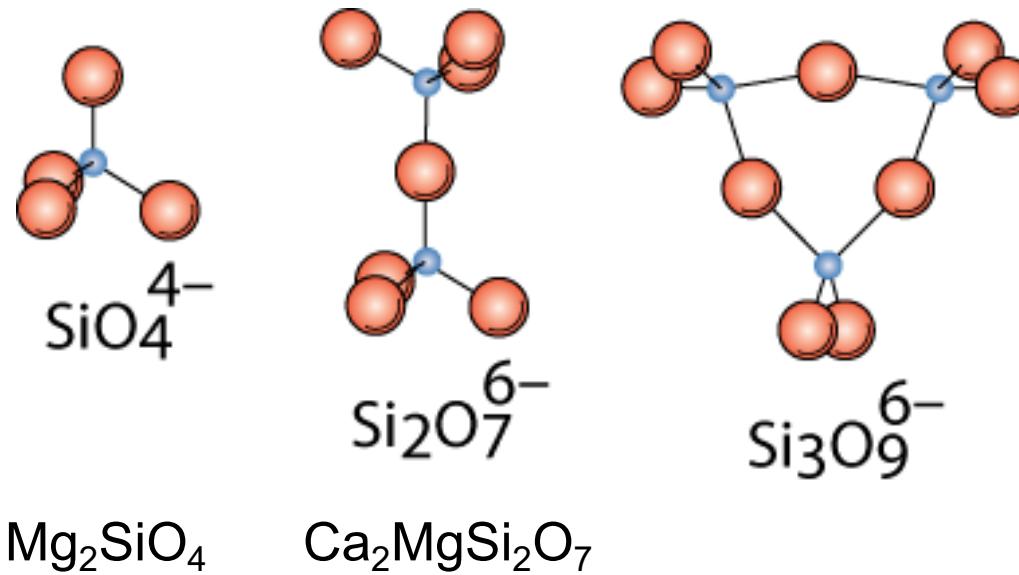
Most common elements on earth are Si & O



- $\text{SiO}_2$  (silica) **polymorphic** forms are quartz, crystobalite, & tridymite
- The strong Si-O bonds lead to a high melting temperature ( $1710^\circ\text{C}$ ) for this material

# Silicates

Bonding of adjacent  $\text{SiO}_4^{4-}$  accomplished by the sharing of common corners, edges, or faces

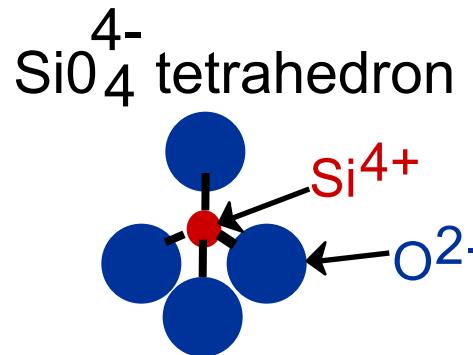


Presence of cations such as  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , &  $\text{Al}^{3+}$

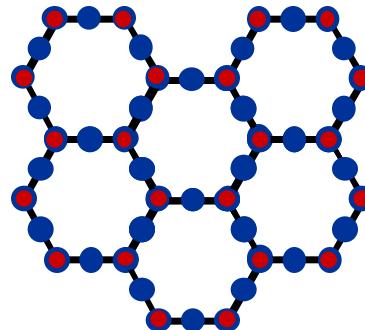
1. maintain charge neutrality, and
2. ionically bond  $\text{SiO}_4^{4-}$  to one another

# Glass structure

- Basic Unit:

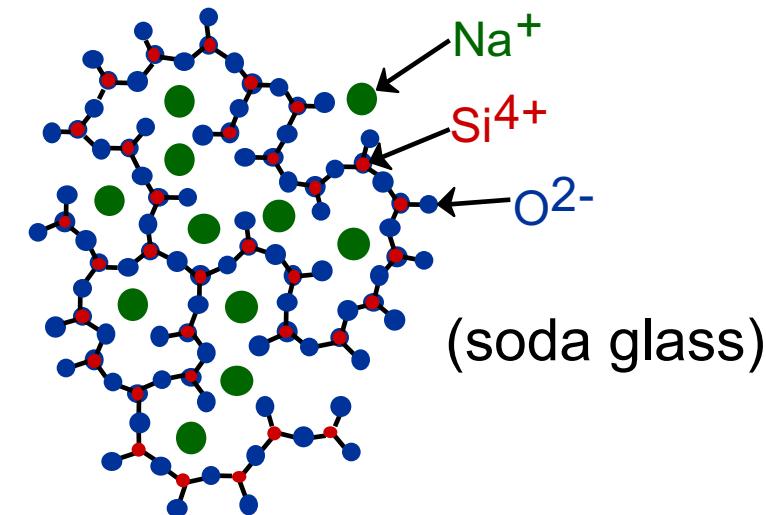


- Quartz is **crystalline**  
 $\text{SiO}_2$ :



Glass is noncrystalline (**amorphous**)

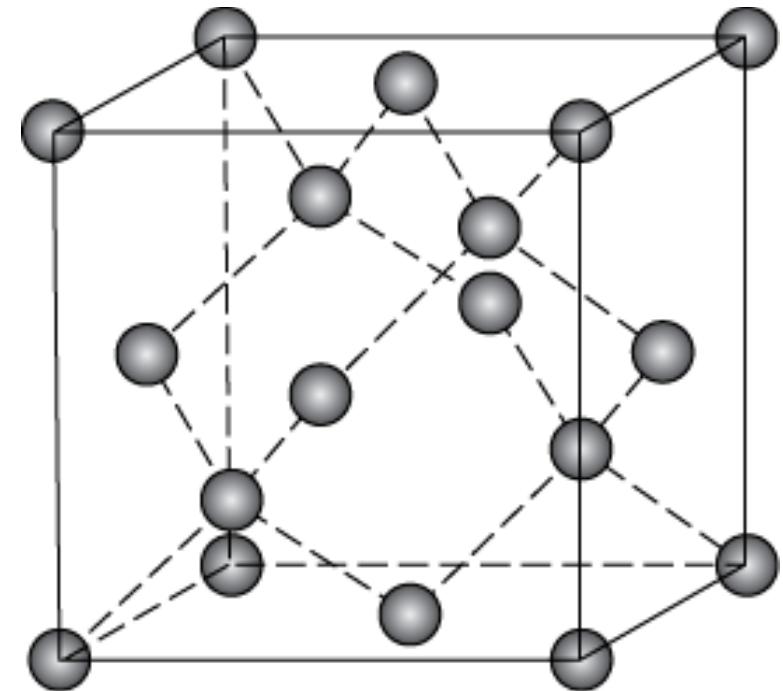
- Fused silica is  $\text{SiO}_2$  to which no impurities have been added
- Other common glasses contain impurity ions such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{B}^{3+}$



# Carbon polymorphs

## Diamond

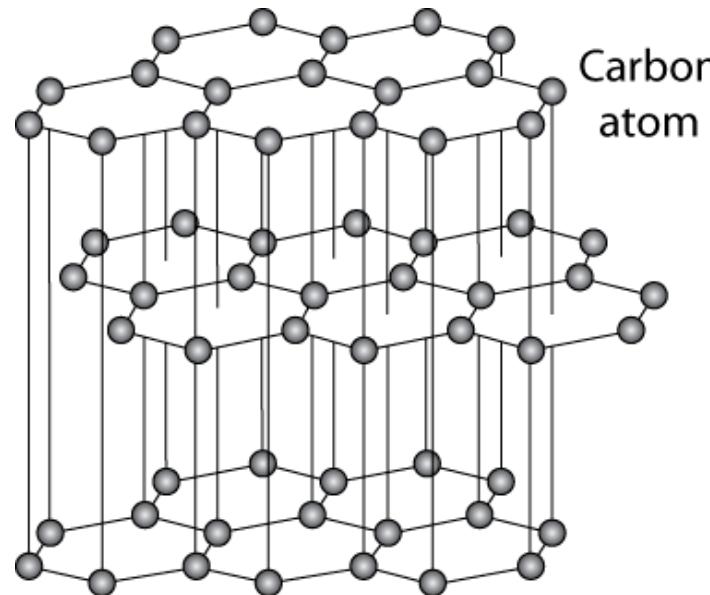
- tetrahedral bonding of carbon
  - hardest material known
  - very high thermal conductivity
- large single crystals – gem stones
- small crystals – used to grind/cut other materials
- diamond thin films
  - hard surface coatings – used for cutting tools, medical devices, etc.



# Carbon polymorphs

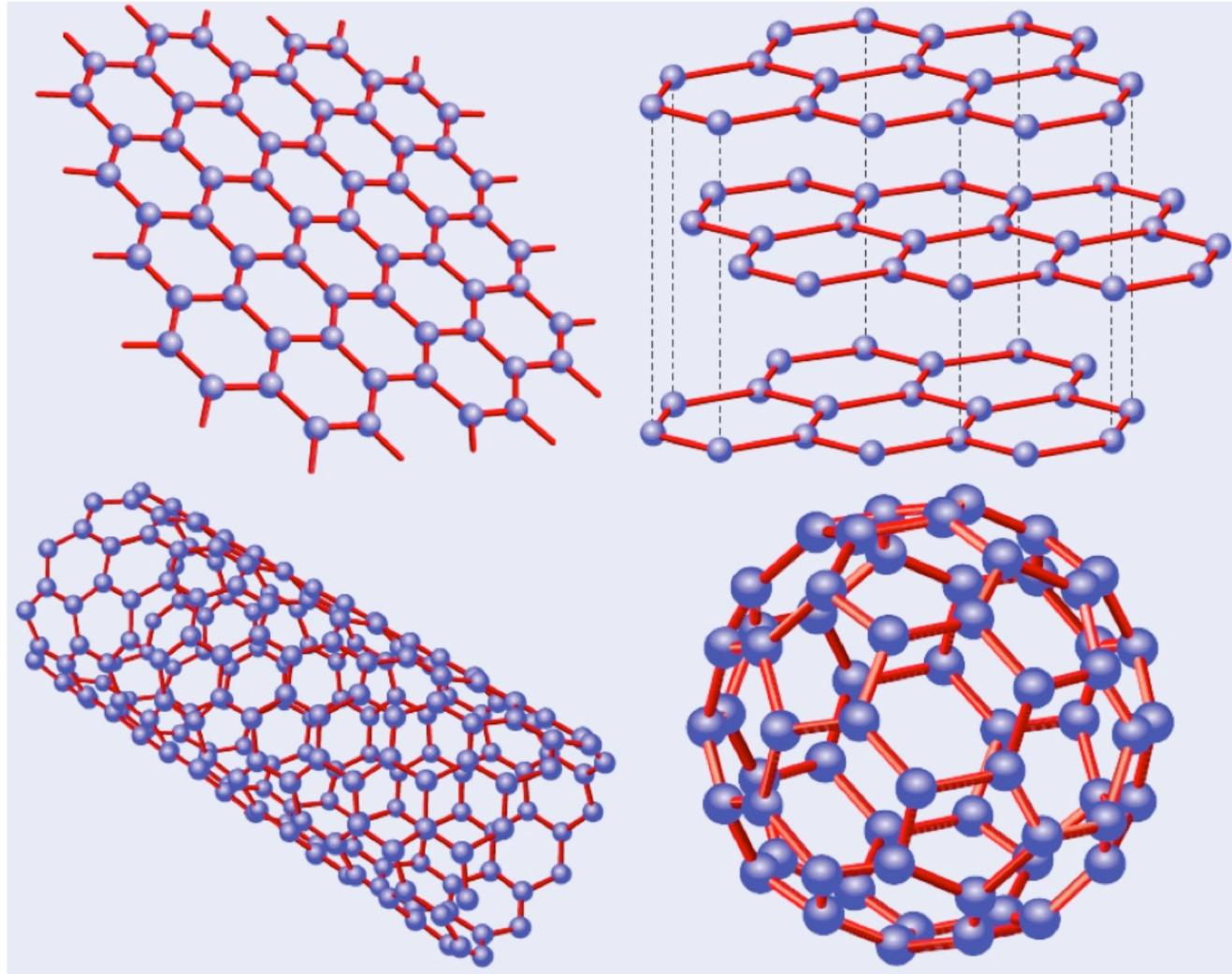
## Graphite

- layered structure – parallel hexagonal arrays of carbon atoms



- weak van der Waal's forces between layers
- planes slide easily over one another -- good lubricant

# Carbon polymorphs



The vocabulary of symmetry and crystallography applies to vastly different structures

# Alloys

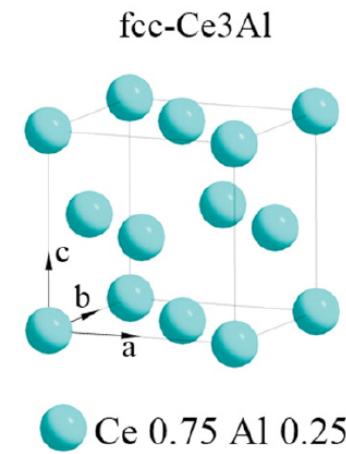
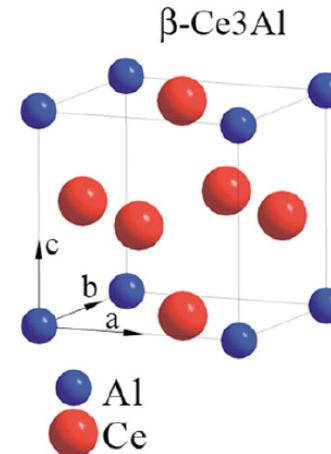
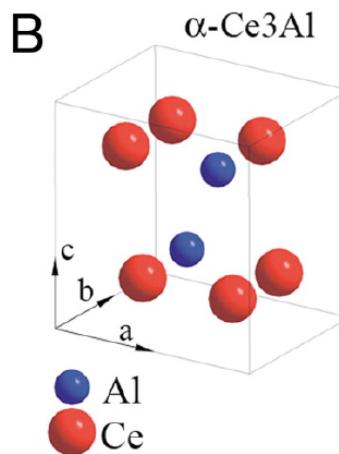
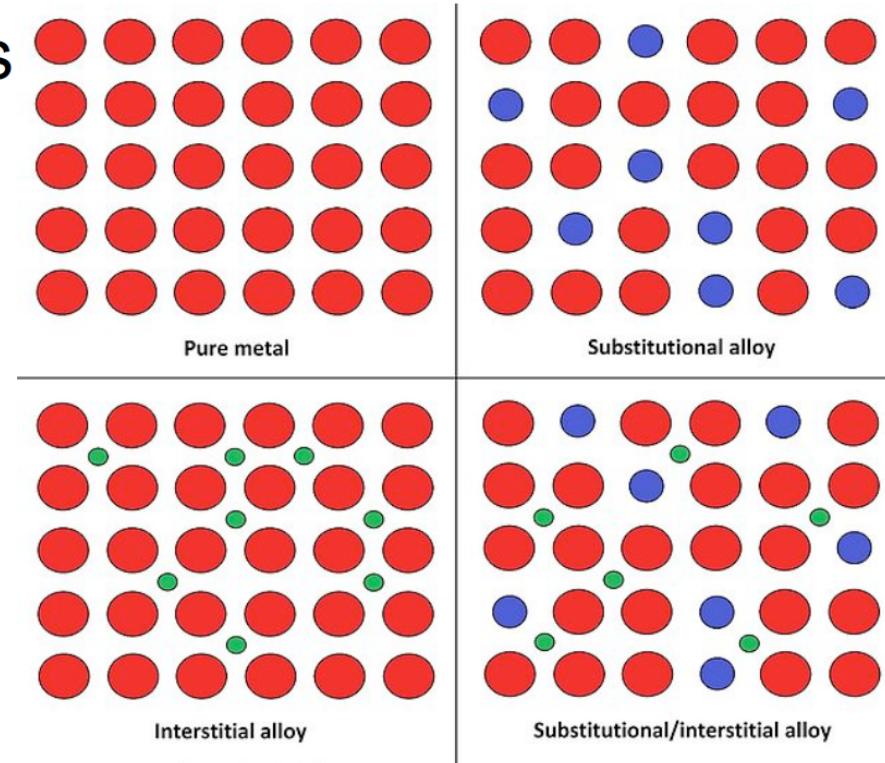
- **Alloys:** mixture of elements  
(usually applied to metals)

- **Disordered alloys**

- Substitutional
- Interstitial

- **Ordered alloys**

- Compounds
- Rarely perfectly ordered
- Solubility



# Summary: Crystallography

- **Terminology:** Lattice, basis, Bravais lattice, translation vectors, basis vectors, unit cell
- **Symmetry elements:** rotations, mirrors, inversions, screw axes, glide planes
- Bravais lattices and their fundamental symmetries, rotation
- Indices for positions, line directions, planes and their families
- Cubic and hexagonal lattices in detail
- Atomic packing factors, atoms per cell, close packed planes and directions
- Ionic solids: Stoichiometry (charge neutrality), anion/cation sizes
- Covalent solids: Bond directionality and basic structural units