

## Chapter 3: Structure of Ceramics

### ISSUES TO ADDRESS...

- Structures of ceramic materials:  
How do they differ from that of metals?

- Define basic terms and give examples of each:
  - Lattice
  - Basis Atoms (Decorations or Motifs)
  - Crystal Structure
  - Unit Cell
  - Coordination Numbers
- Describe hard-sphere packing and identify cell symmetry.

## Bonding in Ceramics

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

CaF<sub>2</sub>: large  
SiC: small

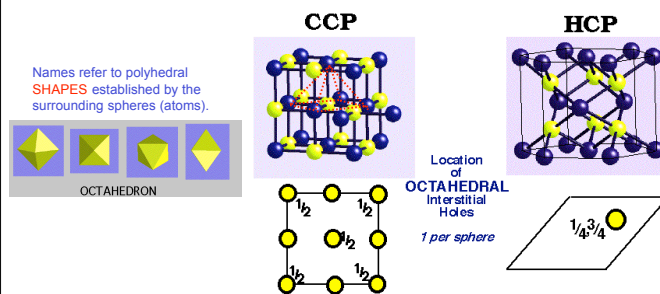
H	Li	Be	B	C	N	O	F	Ne
2.1	1.0	1.5	2.0	2.5	3.0	3.5	4.0	-
Na	Mg	Al	Si	P	S	Cl	Ar	-
0.9	1.2	1.5	1.8	2.2	2.5	3.0	-	-
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co
0.8	1.0	1.3	1.5	1.6	1.8	1.9	2.2	2.5
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh
0.8	1.0	1.3	1.5	1.6	1.8	1.9	2.2	2.5
Cs	Ba	La	Ce	Pr	Nd	Pm	Sm	Eu
0.7	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6
Fr	Ra	Ac	Th	Pa	U	Np	Pu	Am
0.7	0.9	1.0	1.1	1.2	1.3	1.4	1.5	1.6

Table of Electronegativities

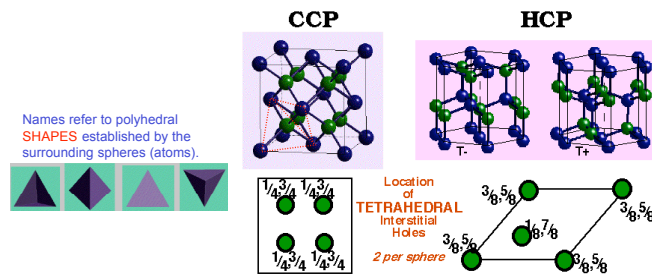
Adapted from Fig. 2.7, Callister 6e. (Fig. 2.7 is adapted from Linus Pauling, *The Nature of the Chemical Bond*, 3rd edition, Copyright 1939 and 1940, 3rd edition. Copyright 1960 by Cornell University.

## Locating OCTAHEDRAL Interstitial Holes

In close-packed arrangements of large atoms (negative anions), the **HOLES** (either **TETRAHEDRAL** or **OCTAHEDRAL**) may be filled with **smaller** atoms of a different sort, which is exactly how ceramics and compounds are created!



## Locating TETRAHEDRAL Interstitial Holes



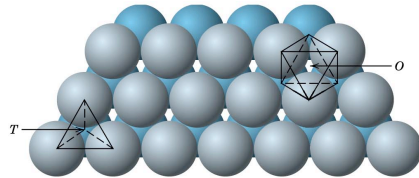
## Ionic Crystals

Most ionic crystals can be considered as close-packed structure of BIG anions with SMALL cations in the interstitial sites (spaces between BIG anions).

Table 3.2

Material	Percent Ionic Character	Cation Radius (nm)	Anion Radius (nm)
CaF <sub>2</sub>	89	0.100	0.133
MgO	73	0.072	0.14
NaCl	67	0.102	0.182
Al <sub>2</sub> O <sub>3</sub>	63	0.053	0.140
SiO <sub>2</sub>	51	0.040	0.140

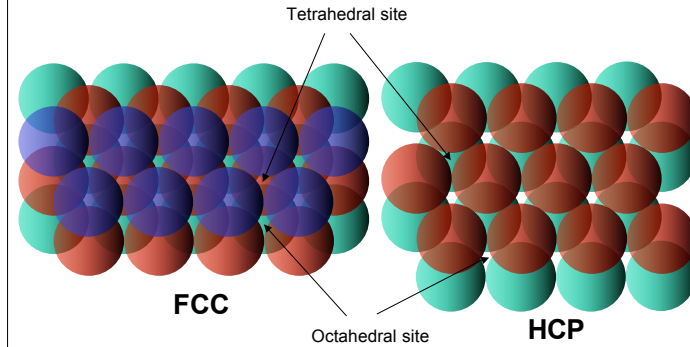
Note: larger anion radius



For "hard sphere" atoms, interstitial size determined by geometry!  
For a given Anion, what Cation will fit in hole?

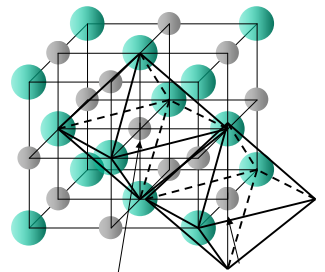
## Tetrahedral and Octahedral Holes in Close-Packed Crystals

See holes: stack pennies in either FCC or HCP and see interstitial sites.



## Interstitial Sites in FCC

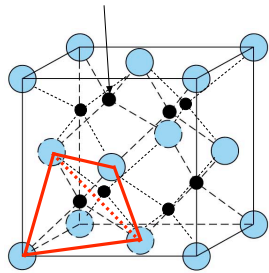
Octahedral ( $O_h$ ) sites



1 at the center  
12 edge sites  
(each shared by 4 cells)

Net 4  $O_h$  sites/unit cell

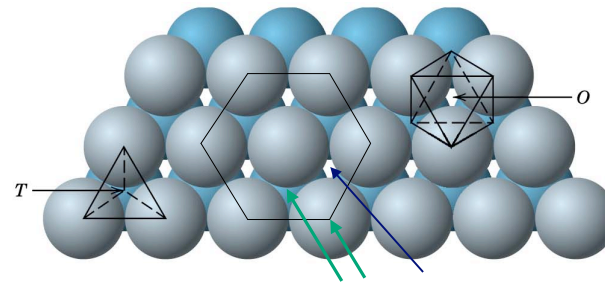
Tetrahedral ( $T_d$ ) sites



Net 8  $T_d$  sites/unit cell

## Interstitial Sites in HCP

Looking down  $[0001]$  of HCP unit cell



3  $O_h$  sites on top half of unit cell (by symmetry, 3 more on bottom half)  
6  $T_d$  sites on top half of unit cell (by symmetry, 6 more on bottom half)

Total 6  $O_h$  sites

Total 12  $T_d$  sites

### Interstitial Sites in HCP

6 atoms in HCP unit cell =  $12 \cdot (1/6) + 3 + 2 \cdot (1/2)$   
corners interior faces

Total 6  $O_h$  sites

(a)

$O_h$  sites form HCP lattice. Hence, sites equal atoms.

Total 12  $T_d$  sites

(b)

$T_d$  sites for 2 HCP lattices. Hence, twice as many sites as atoms.

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### Ionic Structures: Filling in the “holes” between Anions

- Charge Neutrality:**
  - Net charge in structure should be zero.

$$\text{CaF}_2: \text{Ca}^{2+} \text{ cation} + 2 \text{ F}^- \text{ anions}$$

- General form:  $A_m X_p$   
 $m, p$  determined by charge neutrality
- Stable structures:**
  - maximize the # of nearest oppositely charged neighbors.

unstable

stable

stable

Adapted from Fig. 12.1, Callister 6e.  
Fig. 3.4 in text

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### Coordination Number and Ionic Radii

- Coordination # increases with**

**Issue: How many anions can you arrange around a cation?**

$r_{\text{cation}} / r_{\text{anion}}$	Coord #
$< .155$	2
$.155-.225$	3
$.225-.414$	4
$.414-.732$	6
$.732-1.0$	8

**ZnS (zincblende)**  
Adapted from Fig. 12.4, Callister 6e.

**NaCl (sodium chloride)**  
Adapted from Fig. 12.2, Callister 6e.

**CsCl (cesium chloride)**  
Adapted from Fig. 12.3, Callister 6e.

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### Coordination Number and Ionic Radii

- How does geometry determine this?**

Stable

Stable

Unstable

Negative electron density overlaps strongly so unstable

**e.g. 3-atom coordinated**

$r_C$   
Cation

$r_A$   
Anion

here  $\alpha = 30^\circ$

$$\cos \alpha = \cos 30^\circ = \frac{AP}{AO} = \frac{r_A}{r_A + r_C}$$

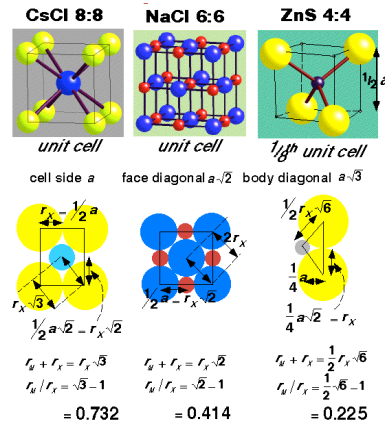
$$\frac{r_C}{r_A} = \frac{1 - \sqrt{3}/2}{\sqrt{3}/2} = 0.155$$

**Minimum cation-anion ratio for 3-atom coordination.**

From Fig. 3.4, show that 6-atom coordinated gives  $r_C/r_A = 0.414$ .

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### 3D Geometry: Limiting Cation/Anion Ratio



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### Example - Predicting AX structures

Using neutrality and ionic radii, what structure is predicted?

- Step 1: Check **Valence** ( $\text{Zn}^{2+}$  and  $\text{S}^{2-}$ ) and **Charge Neutrality**  
 $\text{Zn}^{2+} : \text{S}^{2-} = 1:1$  to get **Formula Unit**  $\Rightarrow \text{ZnS}$

- Consider ZnS:  

$$\frac{r_{\text{Zn}}}{r_{\text{S}}} = \frac{0.074\text{nm}}{0.184\text{nm}} = 0.402$$
From Table 3.4

Based on this ratio,  
 --coord no. CN = 4  
 --anion packing = FCC  
 --structure = Zinc Blende  
From Table 3.5

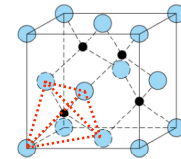


- Result: Must be FCC with only **tetrahedral coordination of cations**.

- How many Anions in cell? 4
- How many Tetrahedral sites? 8
- How many Cations to fill holes? 4
- How do we choose to fill holes? **Reduce Electrostatic Energy**

**This is Zinc Blende Structure**

(other zinc blende materials: ZnTe, CdS, SiC...)



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### Example EXAM QUESTIONS

The zinc blende crystal structure is one that may be generated from close-packed planes of anions.

- Will the stacking sequence be FCC or HCP? Why?
- Will cations fill tetrahedral or octahedral sites? Why?
- What fraction of the positions will be occupied?

This question is concerned with the zinc blende crystal structure in terms of close-packed planes of anions. (See previous slide.)

- The stacking sequence of close-packed planes of anions for the zinc blende crystal structure will be the same as FCC (and not HCP) because the anion packing is FCC (Table 3.5).
- The cations will fill tetrahedral positions since the coordination number for cations is 4 (Table 3.5).
- Only one-half of the tetrahedral positions will be occupied because there are two tetrahedral sites per anion, and yet only one cation per anion.

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### Example of AX structures: Sodium Chloride

Using neutrality ionic radii, what structure is predicted?

- From **Valence** ( $\text{Na}^+$  and  $\text{Cl}^-$ ) and **Charge Neutrality**,  
 $\# \text{Na}^+ \text{ ions} : \# \text{Cl}^- \text{ ions} = 1:1$ , so **NaCl** is formula unit.

- Consider NaCl:  

$$\frac{r_{\text{Na}}}{r_{\text{Cl}}} = \frac{0.102\text{nm}}{0.181\text{nm}} = 0.564$$
From Table 3.4

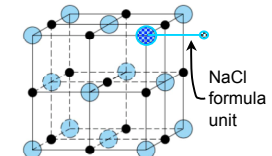
Based on this ratio,  
 --coord no. CN = 6  
 --anion packing = FCC  
 --structure = NaCl  
From Table 3.5



- Result: Must be FCC with **ALL the cation octahedral sites occupied**.

**This is RockSalt Structure**

Other examples are MgO and FeO



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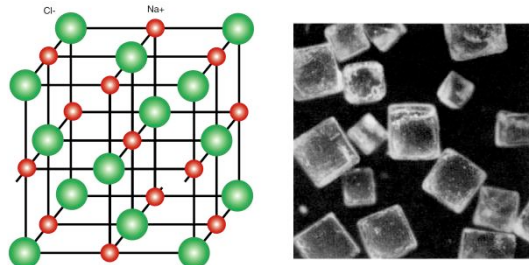
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## Sodium Chloride Structures Observed as Cubes



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## Example of AX structures: Cesium Chloride

Using neutrality and ionic radii, what structure is predicted?

- From **Valence** ( $\text{Cs}^+$  and  $\text{Cl}^-$ ) and **Charge Neutrality**,  $\text{Cs}^+ : \text{Cl}^- = 1:1$ , and **CsCl** is formula unit.

- Consider CsCl :  
From Table 3.4

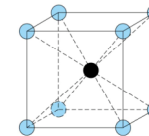
$$\frac{r_{\text{Cs}}}{r_{\text{Cl}}} = \frac{0.170\text{nm}}{0.181\text{nm}} = 0.939$$

Based on this ratio,  
--coord no. CN = 8  
--anion packing = SC  
--structure = CsCl  
From Table 3.5



- Result: Must be CsCl with only **ALL** the cation sites occupied.

This is CsCl Structure



Note: this is similar but is not BCC.

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## Example of $\text{AX}_2$ Structure of Calcium Fluoride

Using neutrality and ionic radii, what structure is predicted?

- From **Valence** ( $\text{Ca}^{2+}$  and  $\text{F}^-$ ) and **Charge Neutrality**,  $\text{Ca}^{2+} : \text{F}^- = 1:2$ , so  **$\text{CaF}_2$**  is formula unit.

- Consider  $\text{CaF}_2$  :

From Table 3.4

$$\frac{r_{\text{Ca}}}{r_{\text{F}}} = \frac{0.100\text{nm}}{0.133\text{nm}} = 0.752$$

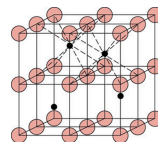
Based on this ratio,  
--coord no. CN = 8  
--anion packing = SC  
--structure = CsCl

From Table 3.5



- Result: Must be CsCl with only **half** the cation sites occupied.

This is Fluorite Structure



Other materials with fluorite structure:  $\text{UO}_2$ ,  $\text{ThO}_2$ ...

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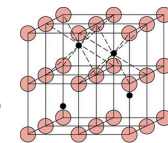


## Note same structures can appear differently $\text{CaF}_2$ with ratio of 1:2 for charge neutrality

Based solely on  $r_{\text{Ca}}/r_{\text{F}} = 0.752$ , the coord. no. is CN=8 for  $\text{Ca}^{2+}$ .

### Option 1

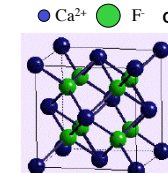
- By arranging F into SC structure, Ca can have CN=8, but with 1 Ca: 2 F only half of the body-centers filled.
- Keep Ca-Ca as far apart as possible! (reduce Coulomb)



Connect F (anions)

### Option 2

- With CN=8 for  $\text{Ca}^{2+}$ , and for  $\text{AX}_2$  where Ca:F is 1:2, F must have CN=  $8/2 = 4$  (or tetrahedral coordination) with Ca. (Careful, this does not always work, e.g.  $\text{ABX}_3$ .)
- Structure for Ca and F in Tetrahedral holes, which is the picture on webnotes (and here).



Connect Ca (cations)

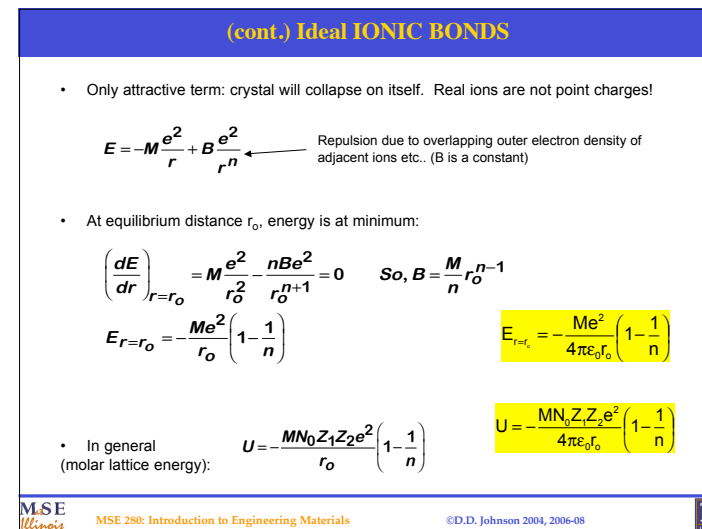
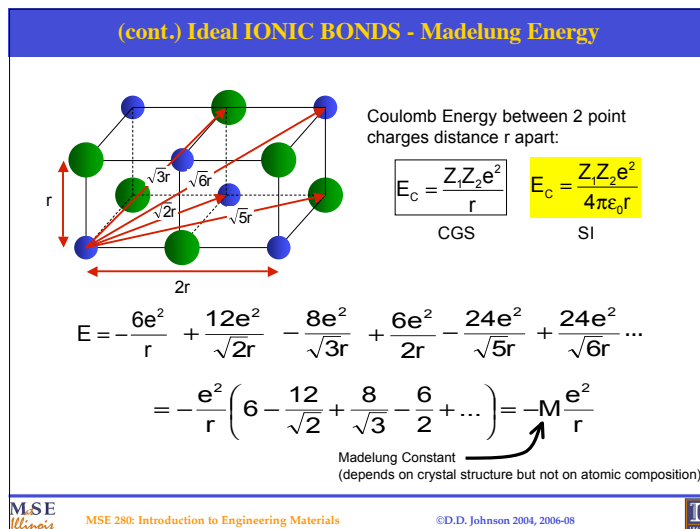
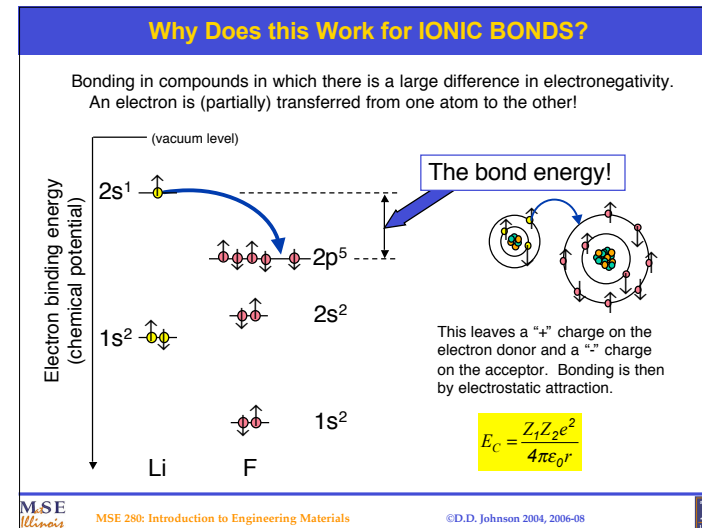
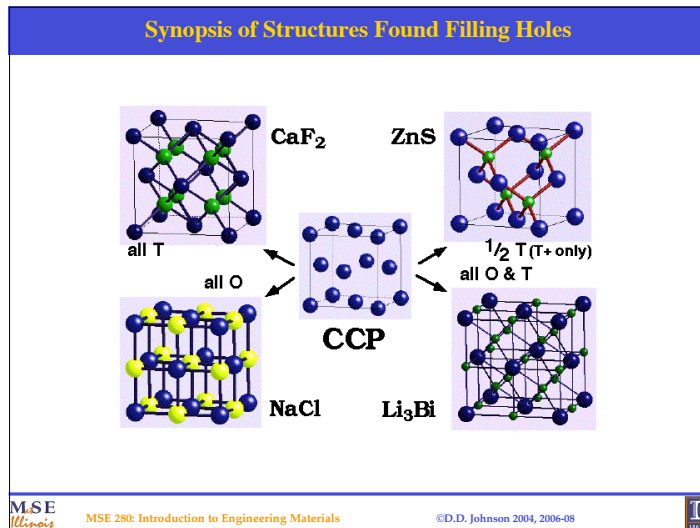
Both top and bottom cells give exactly the same structure, only origin is shifted!

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### (cont.) Compare Systems

Both NaCl and MgO have rock salt structure ( $M = 1.748$ )  
Given:

	$r_o$	$n$	$Z$
NaCl	0.282 nm	9.1	1
MgO	0.210 nm	5.4	2

Calculate lattice energies.

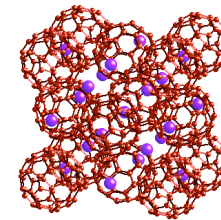
Note:

1. Shorter bond distance (i.e. smaller  $r_o$ ) corresponds to larger lattice energies  $U$  and differing valence.
2. Melting point of NaCl is 801°C whereas MgO has melting point of 2800°C. This difference can be attributed to the lattice energy difference and valence difference.

### $C_{60}$ molecules arrange in a FCC arrangement.

If  $C_{60}$  is reduced with K it forms compounds such as  $K_3C_{60}$ , which is fcc  $C_{60}^{3-}$  with  $K^+$  ions in all octahedral and tetrahedral interstitial sites.

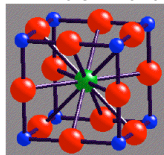
$K_3C_{60}$  is an interesting material because it superconducts at  $T_c = 20$  K and metal fullerenes are the subject of much current research.



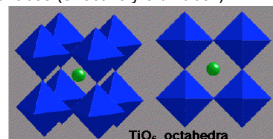
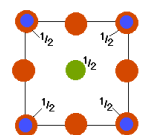
### Example of $A_mB_nX_p$ Structures

#### 1. $ABX_3$ Type (e.g. Calcium titanate $CaTiO_3$ ) Perovskite structure

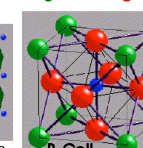
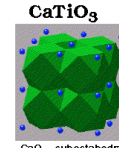
- 1  $Ti^{4+}$  at the center
- 8  $Ca^{2+}$  at the corners (effectively 1/unit cell)
- 6  $O^{2-}$  on the faces (effectively 3/unit cell)



A-Cell



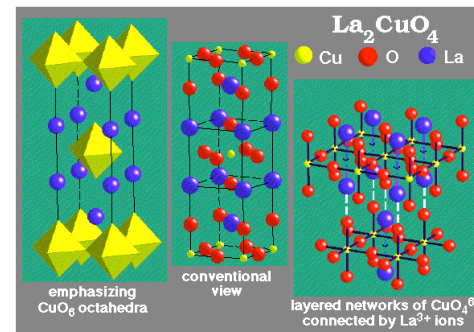
Perovskite  
 $CaTiO_3$



B-Cell

### Example of $A_mB_nX_p$ Structures

#### 2. $AB_2X_4$ Type (e.g. Lanthanum Copper Oxide or $CuLa_2O_4$ )

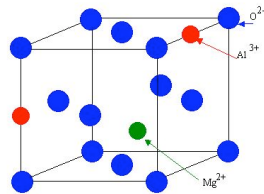


## Example of $A_mB_nX_p$ Structures

### 2. $AB_2X_4$ Type (e.g. Magnesium Aluminate or spinel $MgAl_2O_4$ ) Spinel structure

- FCC of  $O^{2-}$
- $Mg^{2+}$  in tetrahedral sites (1/8 filled)
- $Al^{3+}$  in octahedral sites (half filled)

The mineral Spinel  $Mg^{2+}Al_2^{3+}O_4^{2-}$  is obtained by placing  $O^{2-}$  on an FCC lattice and filling SOME tetrahedral sites with  $Mg^{2+}$  and filling some octahedral sites with  $Al^{3+}$ . The complete unit cell requires 32 O, 16 Al, and 8 Mg atoms to define it.



Partial Unit Cell

## Calculating DENSITY

Simple AB structures:

$$\rho = \frac{n_C A_C + n_A A_A}{N_o V}$$

$n_C$  = number of cations in unit cell  
 $A_C$  = atomic weight of cation  
 $n_A$  = number of anions in unit cell  
 $A_A$  = atomic weight of anion  
 $V$  = volume of unit cell  
 $N_o$  = Avogadro's number

**Example:** Calculate density of NaCl.

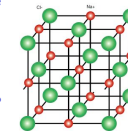
See Text Example

In general:

$$\rho = \frac{\sum_j n_j A_j}{N_o V}$$

Ask yourself –

- What is its formula unit?
- How many formula units?
- How is "a" related to  $r_C$  and  $r_A$ ?
- What is volume of cell?



## Example of Silicate Ceramics

Primarily composed of Si and O

Charge neutrality:  $Si^{4+}:O^{2-}=1:2 \rightarrow SiO_2$

Radii ratio:  $\frac{R_{Si^{4+}}}{R_{O^{2-}}} = \frac{0.040nm}{0.140nm} = 0.286 \rightarrow$  Coordination # = 4 (tetrahedral)

Table 12.3 Ionic Radii for Several Cations and Anions (for a Coordination Number of 6)

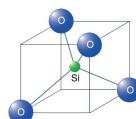
Cation	Ionic Radius (nm)	Anion	Ionic Radius (nm)
$Al^{3+}$	0.053	$Br^{-}$	0.196
$Ba^{2+}$	0.136	$Cl^{-}$	0.181
$Ca^{2+}$	0.100	$F^{-}$	0.133
$Cs^{+}$	0.170	$I^{-}$	0.220
$Fe^{2+}$	0.077	$O^{2-}$	0.140
$Fe^{3+}$	0.069	$S^{2-}$	0.184
$K^{+}$	0.138		
$Mg^{2+}$	0.072		
$Mn^{2+}$	0.067		
$Na^{+}$	0.102		
$Ni^{2+}$	0.069		
$Si^{4+}$	0.040		
$Ti^{4+}$	0.061		

**However:**

% ionic character = 51%  
 (relatively small ionic character  
 significant covalent character exists)

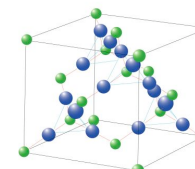
What structure(s) do we expect?

Tetrahedral Silica unit

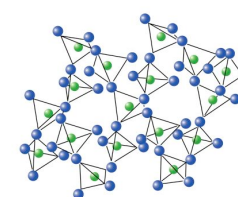


## Crystalline Silica

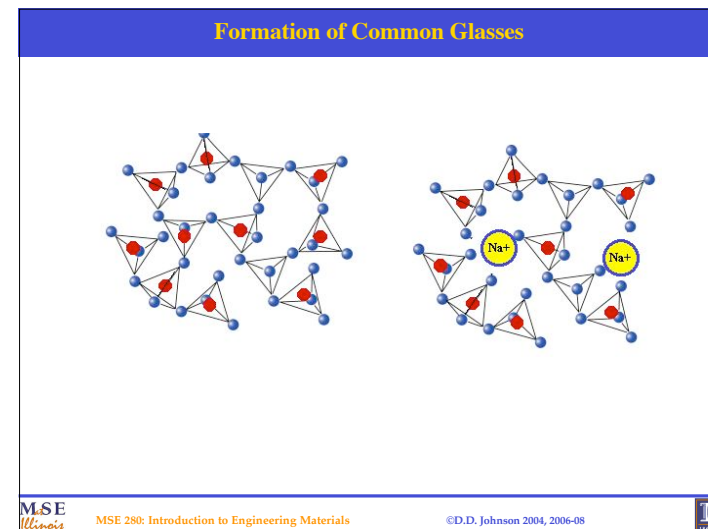
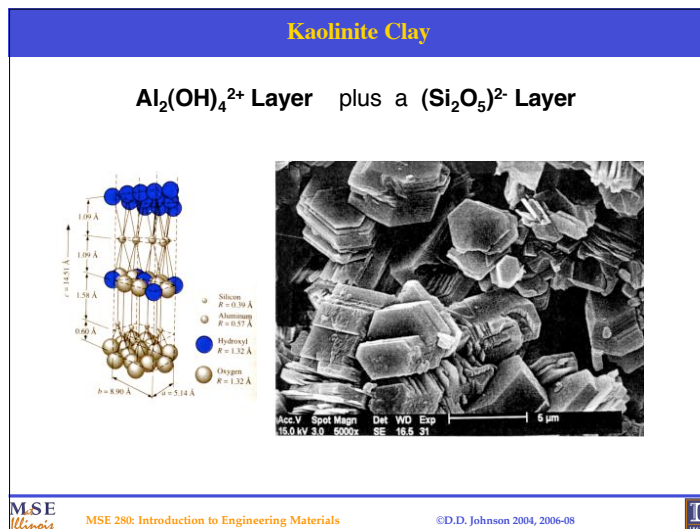
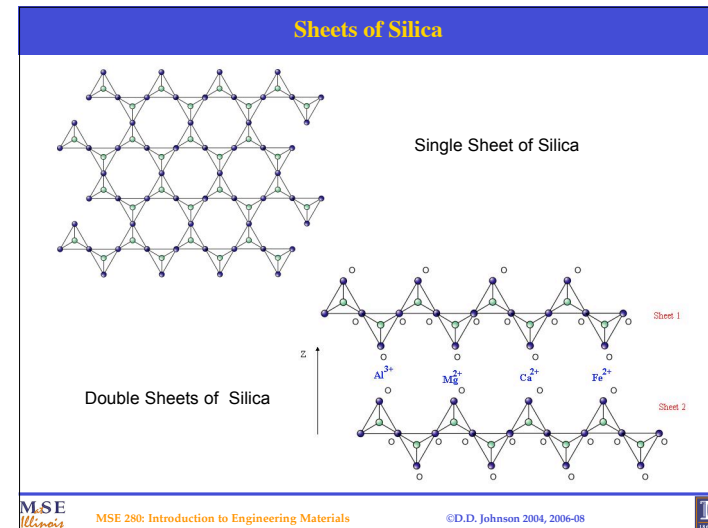
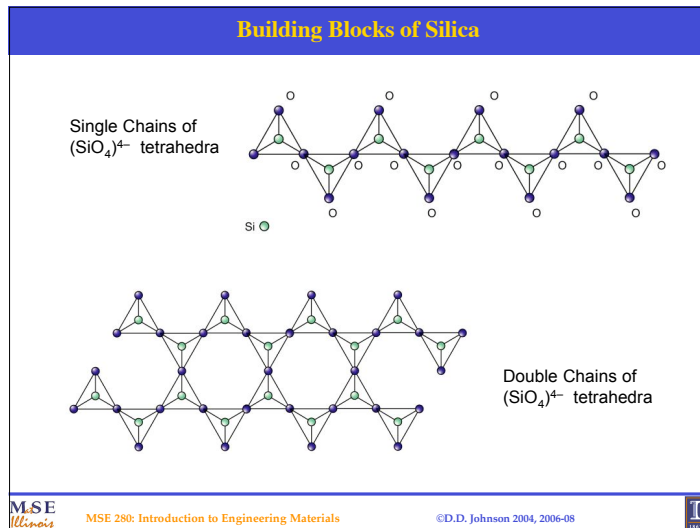
Cristobalite,  $SiO_2$



Quartz



Each O atom is shared by two tetrahedral units

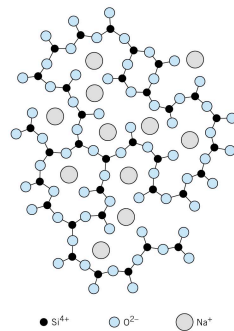


## Silicate Glasses

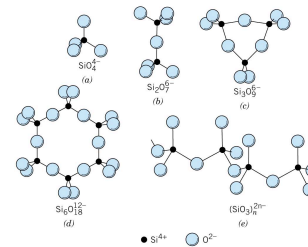
Amorphous silica forms a "network" with relatively large open areas where foreign atoms and particles may be easily introduced.

**Silicates:** amorphous silica with impurities

Sodium-silicate glass

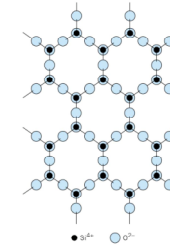


## Silicate Glasses

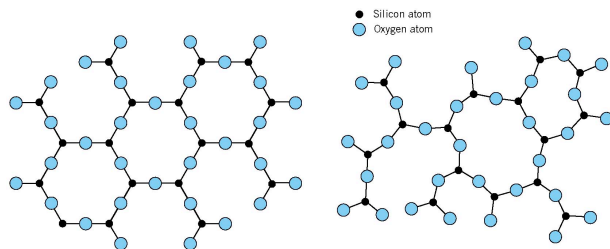


Five Silicate Ion Structures From  $(\text{SiO}_4)^{4-}$  tetrahedra.

2D Silicate sheets  $(\text{Si}_2\text{O}_5)^{2-}$



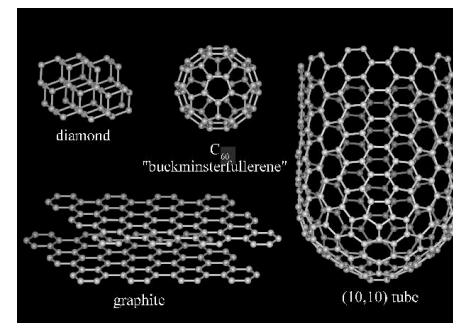
## Crystalline and Non-Crystalline Silica



Relatively open structure but large bond strength  
(e.g. quartz: density =  $2.65 \text{ g/cm}^3$ , mp =  $1710^\circ\text{C}$ )

Non-crystalline: fused silica or vitreous silica

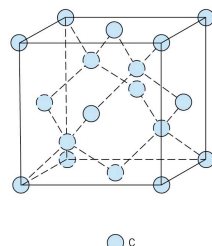
## Carbon Based




Allotropes: different structures for one substance (usually in elemental solids)

Not so easily classified as ceramics, metals or semiconductors....

## Diamond



**FIGURE 12.16**  
Scanning electron micrograph of a diamond thin film in which is shown numerous multifaceted microcrystals. 1000X. (Photograph courtesy of the Norton Company.)



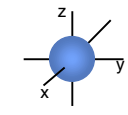
C

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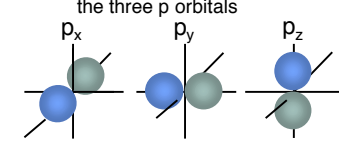
## RECALL: hybrid orbitals are responsible.

**Atomic Orbitals**

an s-orbital

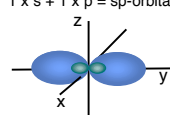


the three p orbitals



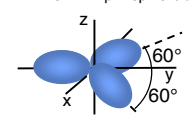
**Hybridization**

$1 \times s + 1 \times p = sp$ -orbitals

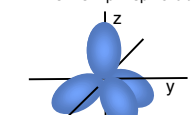


Hybridization for graphitic carbon

$1 \times s + 2 \times p = sp^2$ -orbitals



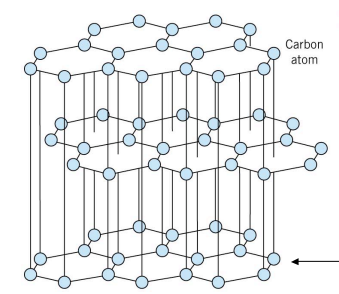
$1 \times s + 3 \times p = sp^3$ -orbitals



Hybridization for Diamond

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**FIGURE 12.17** The structure of graphite.

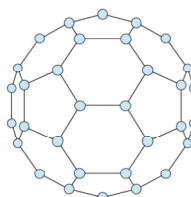


Carbon atom

Graphene: single atomic sheet of graphitic carbon

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## Carbon Nanotubes



C60: Buckey Ball

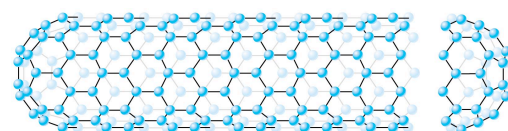
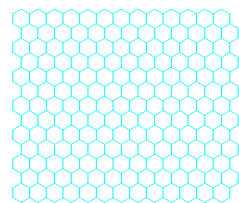


FIGURE 12.19 The structure of a carbon nanotube. (Reprinted by permission from *American Scientist*, magazine of Sigma Xi, The Scientific Research Society. Illustration by Aaron Cox/American Scientist.)

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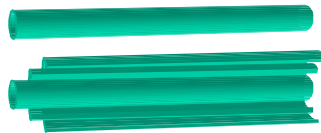
## Carbon Nanotubes



graphene



Carbon nanotube = "rolled up" graphene

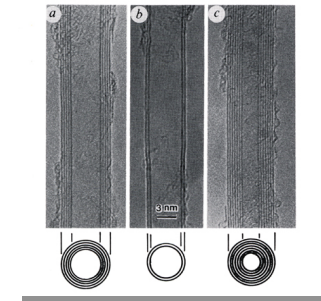


Single-Walled Carbon nanotube  
~<0.7 - 5 nm diameter

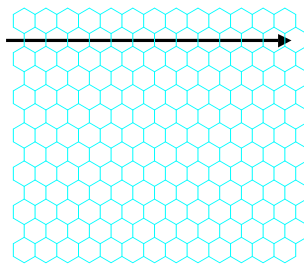
Multi-Walled Carbon nanotube  
> 2 nm diameter (can be larger  
than 100 nm)

## Carbon Multiwall Nanotubes

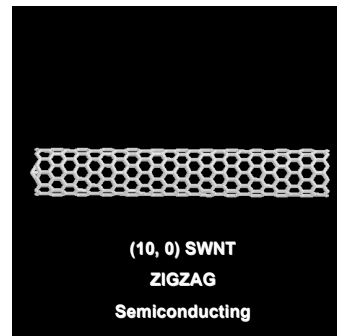
First "observed" (correctly described)  
by Iijima in soot resulting from arc  
discharge of graphite:  
*Nature* **354**, 56 (1991)



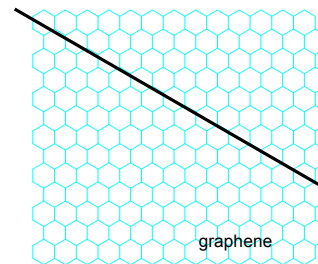
## Metallic Carbon Nanotubes



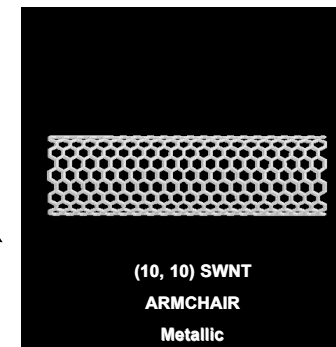
graphene



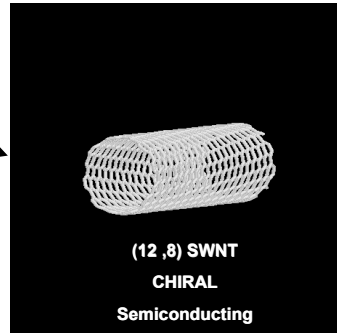
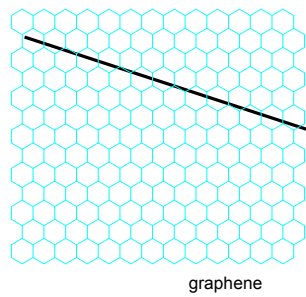
## Metallic Carbon Nanotubes



graphene



## Metallic Carbon Nanotubes



## SUMMARY --- Ionic crystals

- How to predict:
  - Interstitial sites (it's just geometry!)
  - Ionic radii ratios (it's just geometry!)
  - Structures (it's mostly valence and  $R_C/R_A$ )
  - Lattice energy (it's mostly Madelung energy)
- Silica & silicates. (valence and bonds)
- Carbon (diamond, graphite, fullerenes).