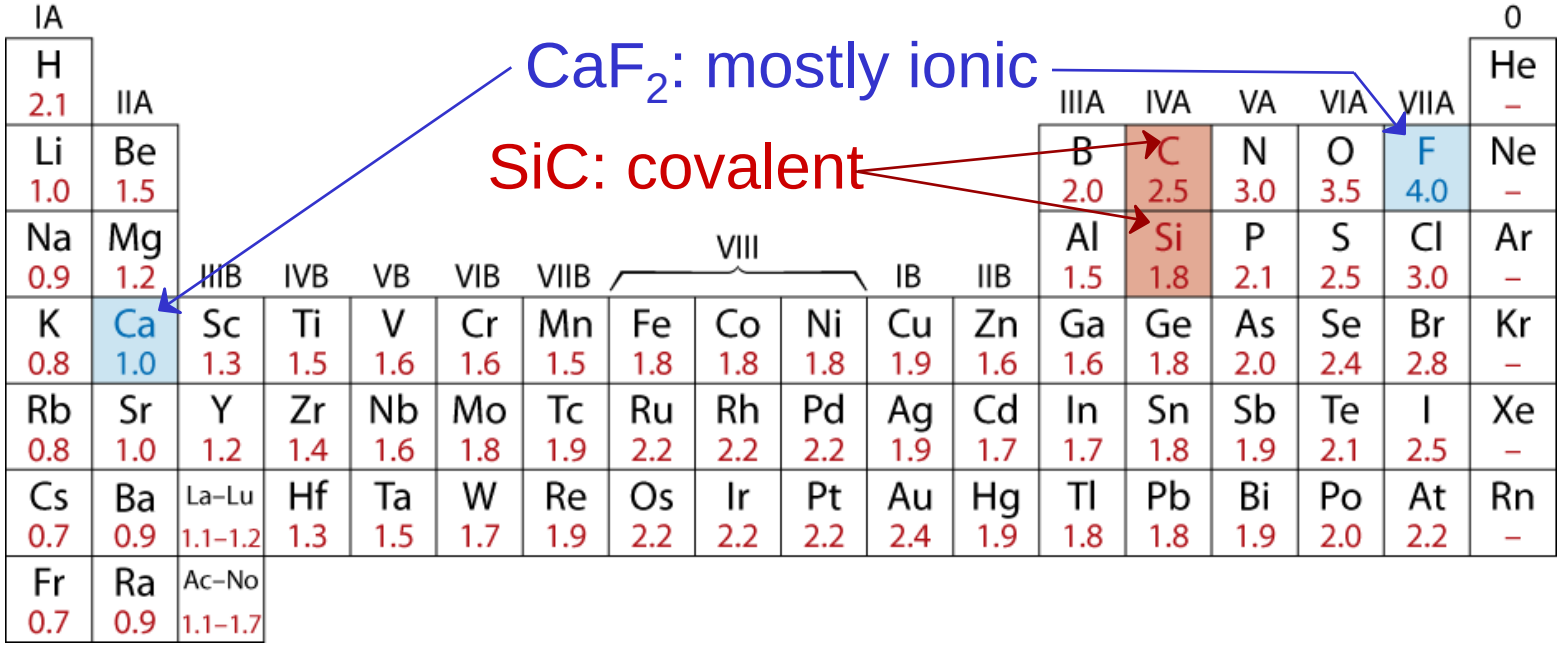
Chapter 12: Structures & Properties of Ceramics

ISSUES TO ADDRESS...

- Bonding and structure of ceramic materials as compared with metals

Atomic Bonding in Ceramics

- Bonding:
  -- Can be ionic and/or covalent in character.
  -- % ionic character increases with difference in electronegativity of atoms.
- Degree of ionic character may be large or small (i.e., mostly covalent):



Adapted from Fig. 2.7, *Callister & Rethwisch 8e.* (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.)

Ceramic Crystal Structures

General considerations of structures for many (**not all!**) ceramics with ionic bonding

- Anions (e.g., O^{2-}, F^{-}, Cl^{-}) **usually** (**but NOT always**) larger than metal cations
  - Close packed anions in a lattice (usually FCC packing)
  - Cations fit into interstitial sites among anion

Factors that Determine Crystal Structure

1. Maximize the # of oppositely charged ion neighbors (or CN)

- CN depends on **relative sizes of ions:**

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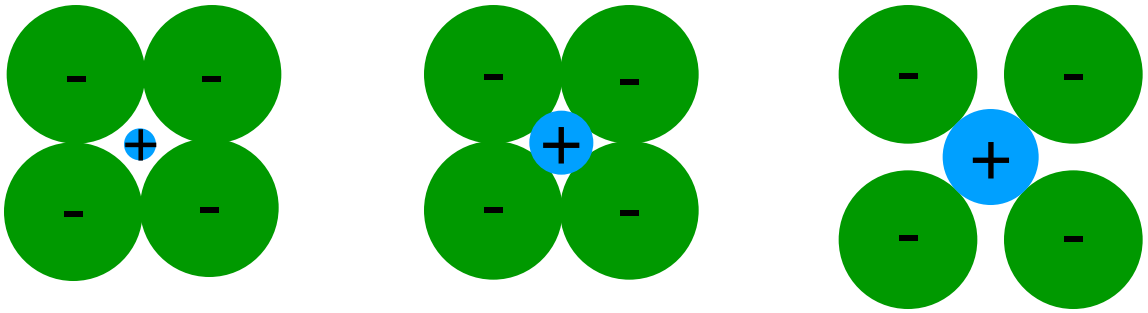
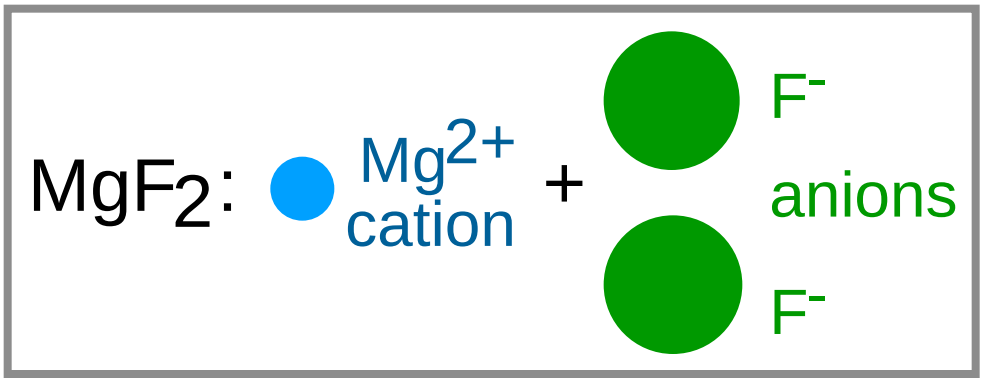


Adapted from Fig. 12.1, *Callister & Rethwisch 8e.*

2. Maintenance of **charge neutrality** :

--Net charge in a ceramics should be zero.

--Reflected in chemical formula:



$A_m X_p$

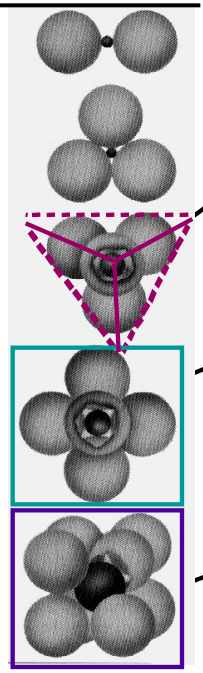
m, p values to achieve charge neutrality

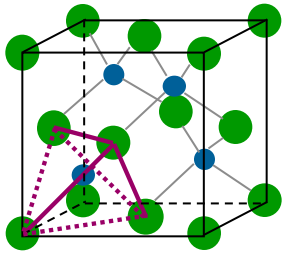
Coordination # and Ionic Radii Ratio

- Coordination # (CN) for cation increases with size ratio of $\frac{r_{cation}}{r_{anion}}$

To form a stable structure, how many anions would surround around a cation?

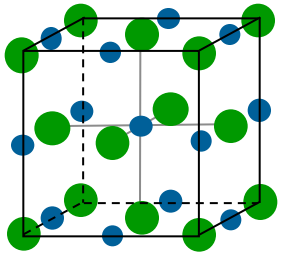
$\frac{r_{cation}}{r_{anion}}$	CN	
< 0.155	2	linear
0.155 - 0.225	3	triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.0	8	cubic
> 1.0	12	





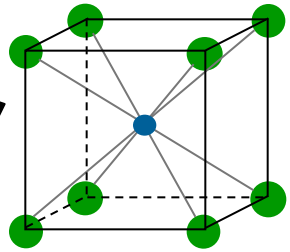
e.g.: ZnS (zinc blende)

Adapted from Fig. 12.4, *Callister & Rethwisch 8e.*



e.g.: NaCl (sodium chloride)

Adapted from Fig. 12.2, *Callister & Rethwisch 8e.*



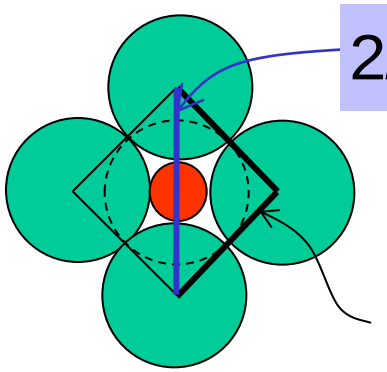
e.g.: CsCl (cesium chloride)

Adapted from Fig. 12.3, *Callister & Rethwisch 8e.*

Adapted from Table 12.2, *Callister & Rethwisch 8e.*

Extra: Determination of Critical Cation to Anion Radius Ratio (Will NOT be examed)

Example for determining critical r_{cation}/r_{anion} for an **octahedral** site with CN = 6



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

$$a = 2r_{anion}$$

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

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

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

Example Problem: Predicting the Crystal 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

Data from Table 12.3, *Callister & Rethwisch 8e.*

- Answer:

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

based on this ratio,
-- coord # = 6 because

$$0.414 < 0.550 < 0.732$$

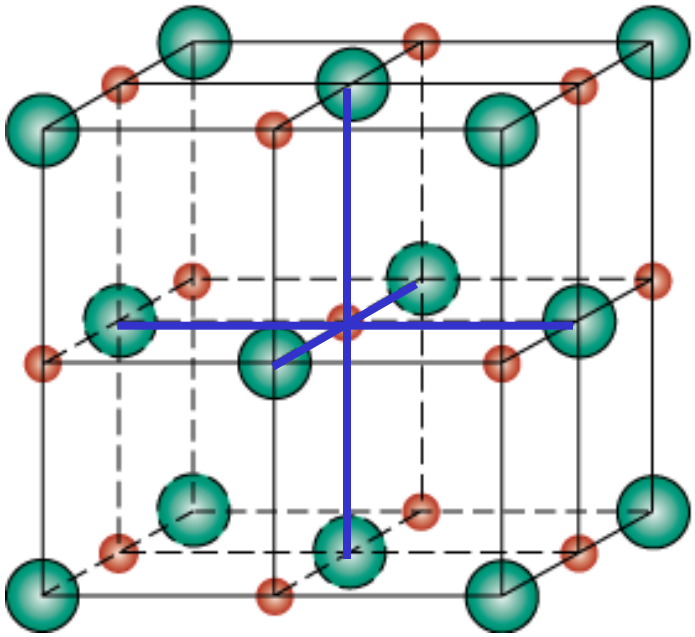
-- crystal structure is NaCl (rocksalt) type

Rock Salt (NaCl type) Structure

For NaCl (rock salt) structure

r_{Na} = 0.102 nm

r_{Cl} = 0.181 nm



Adapted from Fig. 12.2,
Callister & Rethwisch 8e.

r_{Na}/r_{Cl} = 0.564

∴ Since 0.414 < 0.565 < 0.732 octahedral (CN=6) sites preferred for Na^+

Q:

1) Does this CN number make sense based on the unit cell structure given?

2) Within one unit cell what are the averaged numbers of Na and Cl atoms?

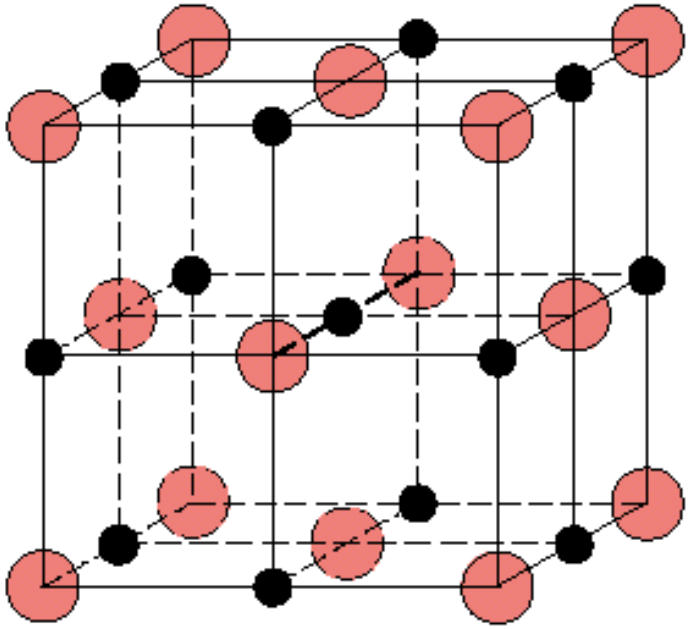
4 Na, 4Cl

3) What is the chemical formula?

NaCl

MgO

MgO also has the NaCl structure



Adapted from Fig. 12.2, *Callister & Rethwisch 8e.*

O^{2-} $r_O = 0.140$ nm

Mg^{2+} $r_{Mg} = 0.072$ nm

$r_{Mg}/r_O = 0.514$

$\therefore$ cations prefer octahedral sites

$\therefore$ Since 0.414 < 0.514 < 0.732 octahedral (CN=6) sites preferred

So each Mg^{2+} (or Fe^{2+}) has 6 neighbor oxygen atoms

Q:

1) Does this CN number make sense based on unit cell structure given?

2) Within one unit cell, what are the averaged numbers of Mg and O atoms?

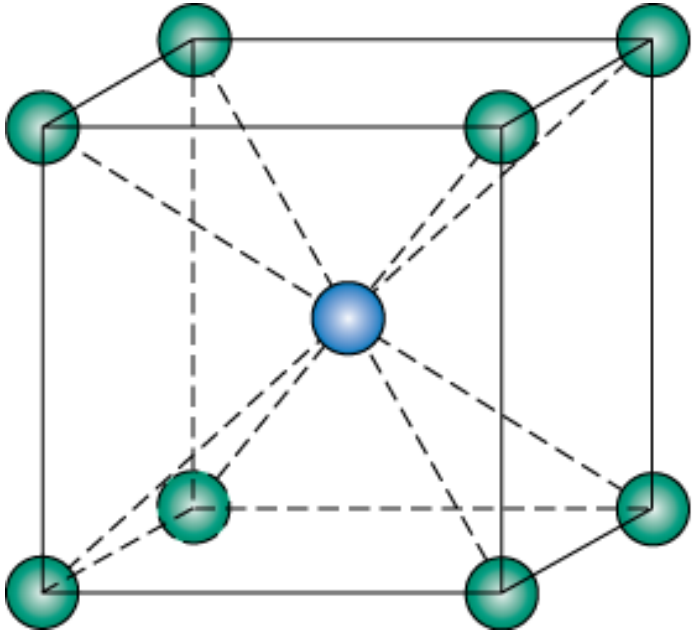
4Mg, 4O

3) What is the chemical formula?

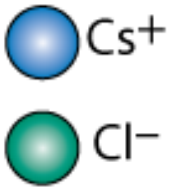
MgO

CsCl Type Crystal Structures

Cesium Chloride structure:



Adapted from Fig. 12.3,
Callister & Rethwisch 8e.



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

$\therefore$ Since 0.732 < 0.939 < 1.0, cubic sites preferred

So each Cs^+ has 8 neighbor Cl^-

Q:

1) Does this CN number make sense based on unit cell structure given?

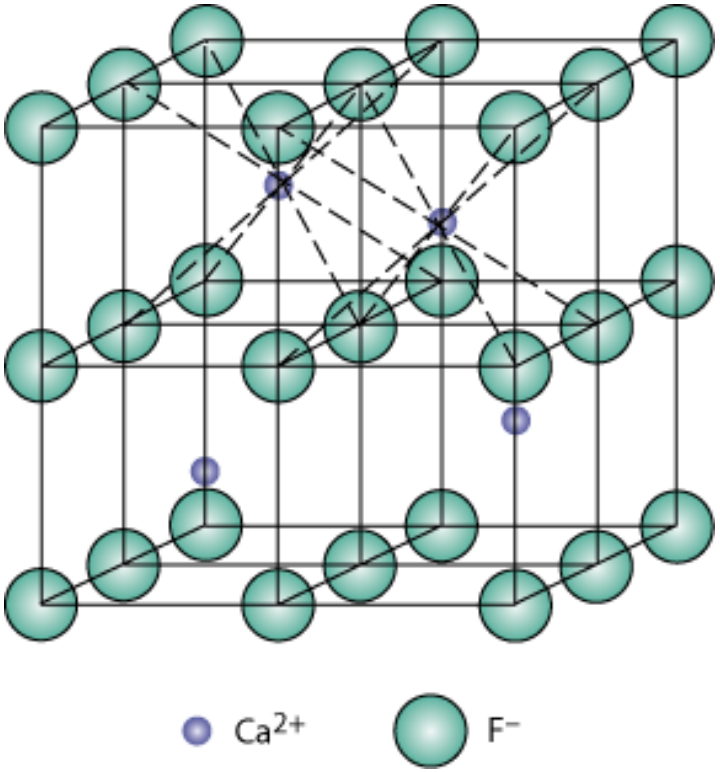
2) Within one unit cell, what are the averaged numbers of Cs and Cl atoms ?

1 Cs, 1 Cl

3) What is the chemical formula?

CsCl

Fluorite (CaF_2 type) Crystal Structures



Adapted from Fig. 12.5,
Callister & Rethwisch 8e.

- Calcium Fluorite (CaF_2 type)
- Cations in cubic sites
- UO_2, ThO_2, ZrO_2, CeO_2

Q:

1) Does this CN number make sense based on unit cell structure given?

2) Within one unit cell, what are the averaged numbers of Ca and F atoms ?

4 Ca, 8 F

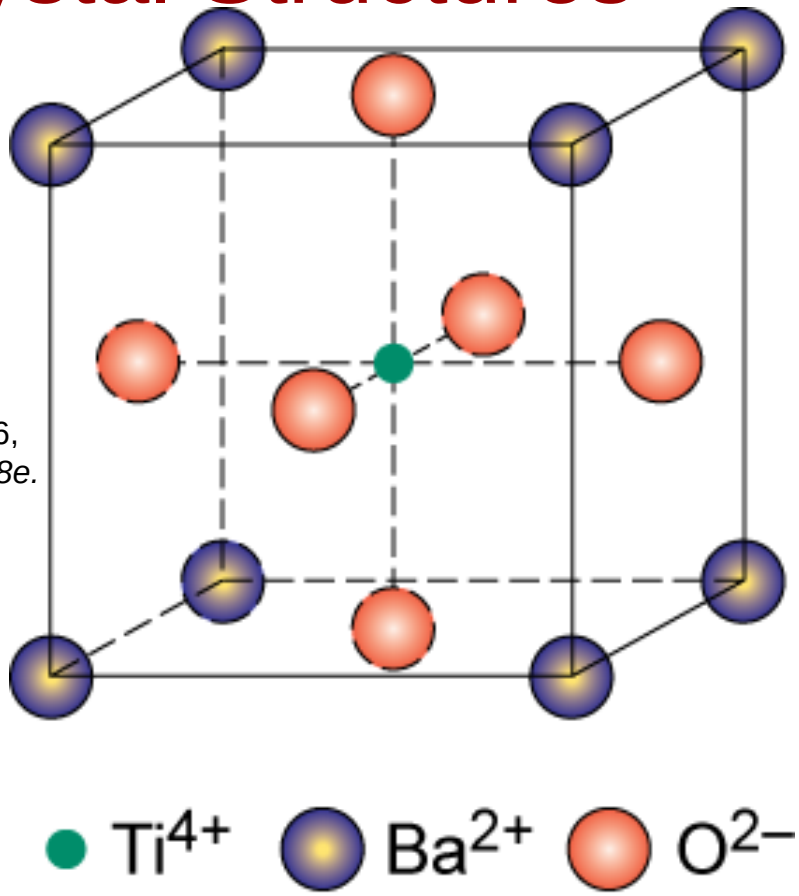
3) What is the chemical formula?

CaF2

Perovskite Crystal Structures

- Perovskite structure

Ex: complex oxide



Adapted from Fig. 12.6, *Callister & Rethwisch 8e.*

Q:

1) What is the CN number based on unit cell structure given for Ti^{4+} ?

CN (Ti^{4+}) = 6

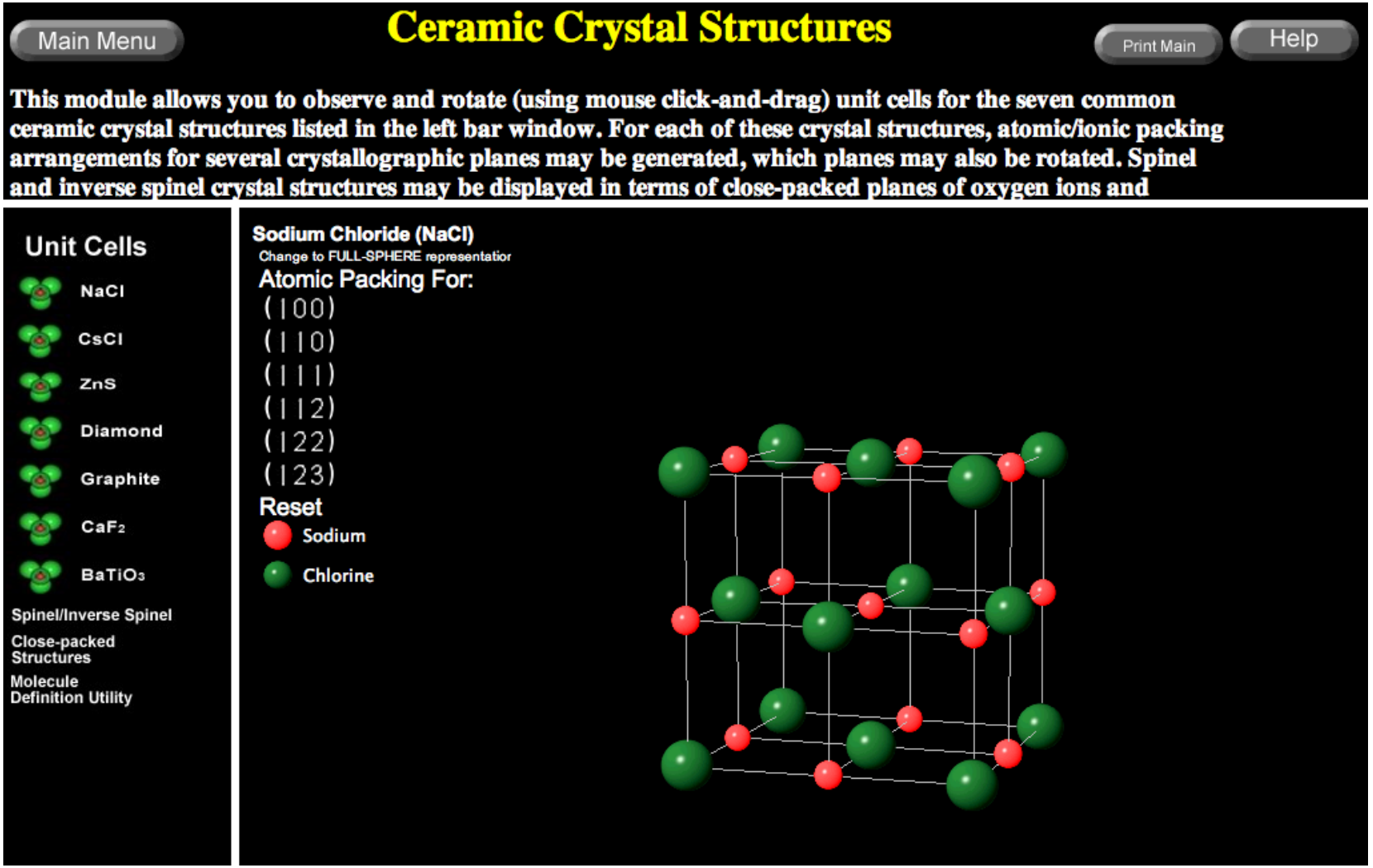
2) Within one unit cell, what are the averaged numbers of Ba, Ti, and O atoms ?

1 Ba (hint: 8x1/8 = 1), 1 Ti (hint: one in unit cell center) , 3 O (hint: 6 * ½ = 3),

3) What is the chemical formula?

$BaTiO_3$

VMSE: Ceramic Crystal Structures



Density Computations for Ceramics

Number of formula units/unit cell

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

Avogadro's number

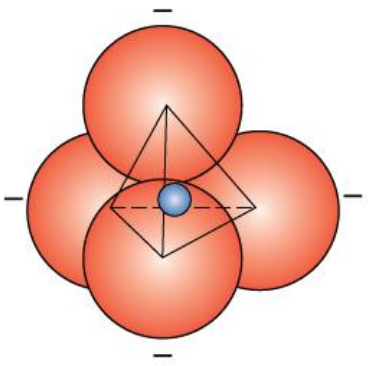
Volume of unit cell

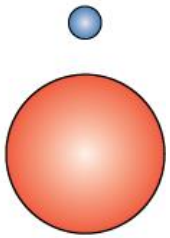
ΣA_C = sum of atomic weights of all cations in formula unit

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

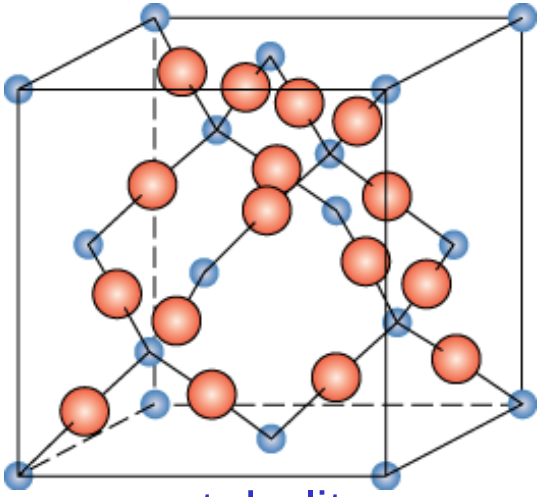
Silicate Ceramics

Most common elements on earth are Si & O





Adapted from Figs. 12.9-10, *Callister & Rethwisch 8e*



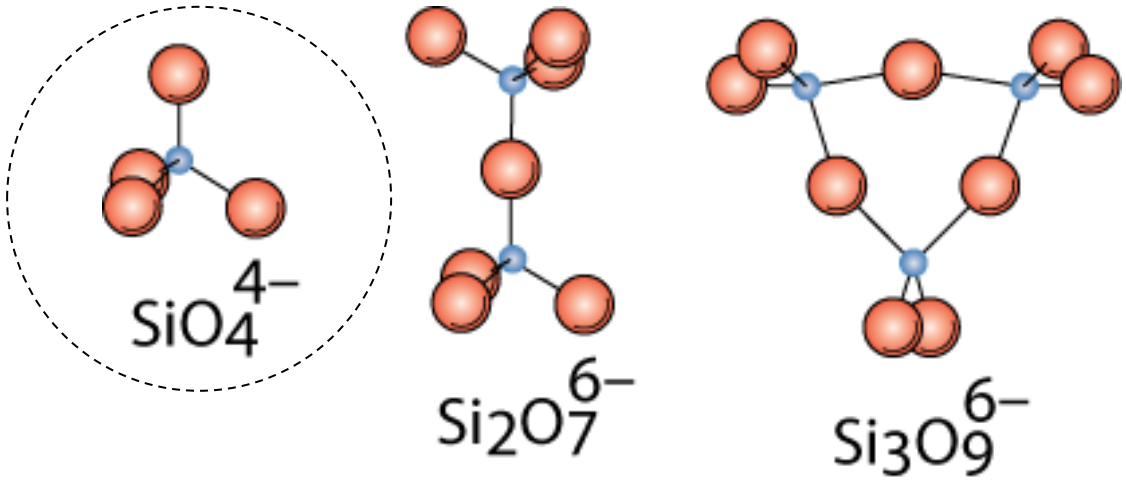
crystobalite

- SiO_2 (silica) polymorphic forms are quartz, crystobalite, & tridymite
- The strong Si-O bonds lead to a high melting temperature (1710ºC) for this material

Silicates

Bonding of adjacent SiO_4^{4-} accomplished by the sharing of common corners, edges, or faces

Basic building block



Adapted from Fig. 12.12, *Callister & Rethwisch 8e.*

Mg_2SiO_4 $Ca_2MgSi_2O_7$

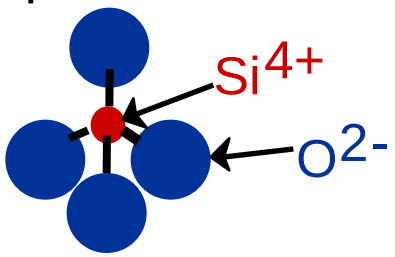
Presence of cations such as Ca^{2+}, Mg^{2+}, & Al^{3+}

1. maintain charge neutrality, and
2. ionically bond SiO_4^{4-} to one another

Glass Structure

- Basic Unit:

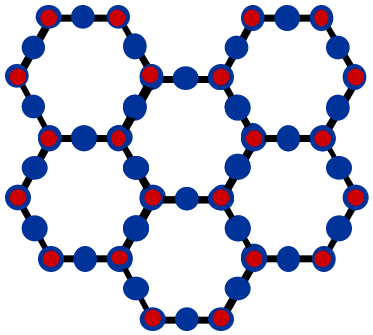
SiO_4^{4-} tetrahedron

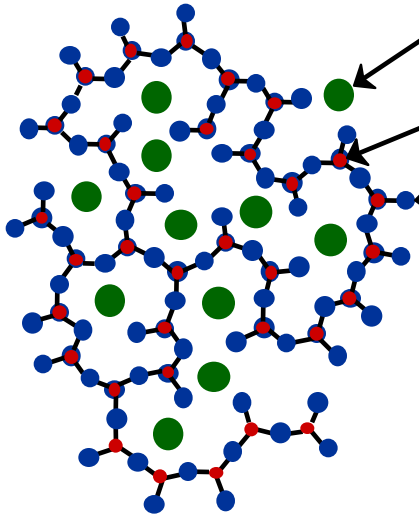


Glass is noncrystalline (amorphous)

- Fused silica is SiO_2 to which no impurities have been added
- Other common glasses contain impurity ions such as Na^+, Ca^{2+}, Al^{3+}, and B^{3+}

- Quartz is crystalline SiO_2:





(soda glass)

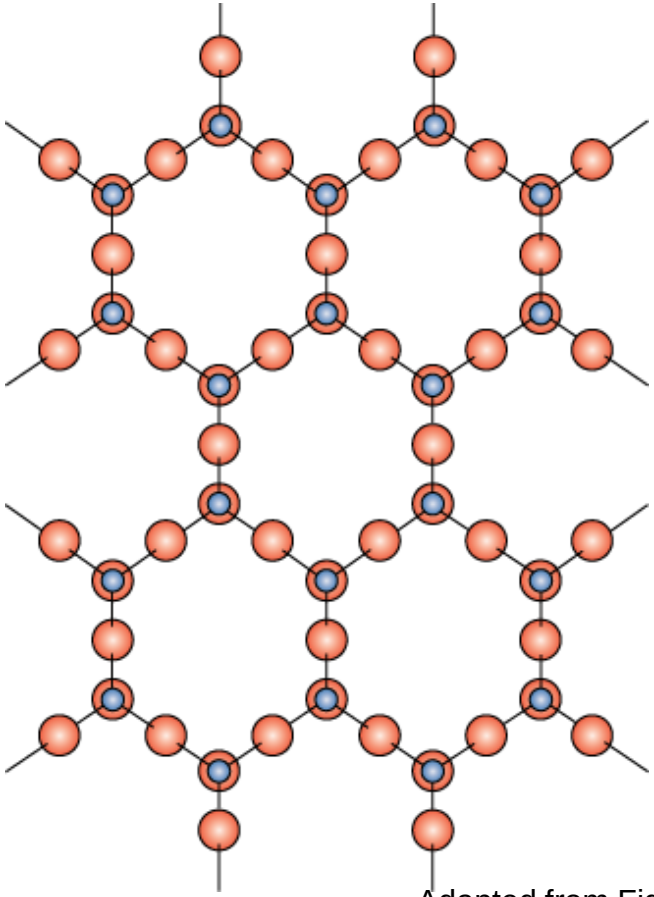
Adapted from Fig. 12.11, *Callister & Rethwisch 8e*.

Layered Silicates

- Layered silicates (e.g., clays, mica, talc)
  - SiO_4 tetrahedra connected together to form 2-D plane

- A net negative charge is associated with each $(Si_2O_5)^{2-}$ unit
  - Each hexagon has 6 Si corner, but each Si can be counted only as 1/3 therefore, 6 x 1/3 = 2 Si
  - Two types of oxygen:
    - 6 O, one on each side of the hexagon, counted as ½, therefore 6x ½ = 3
    - 6 O, each along the three-cell edge, counted as 1/3, therefore, 6x1/3 = 2
    - Totally: 3+2 = 5 per unit (hexagonal) cell

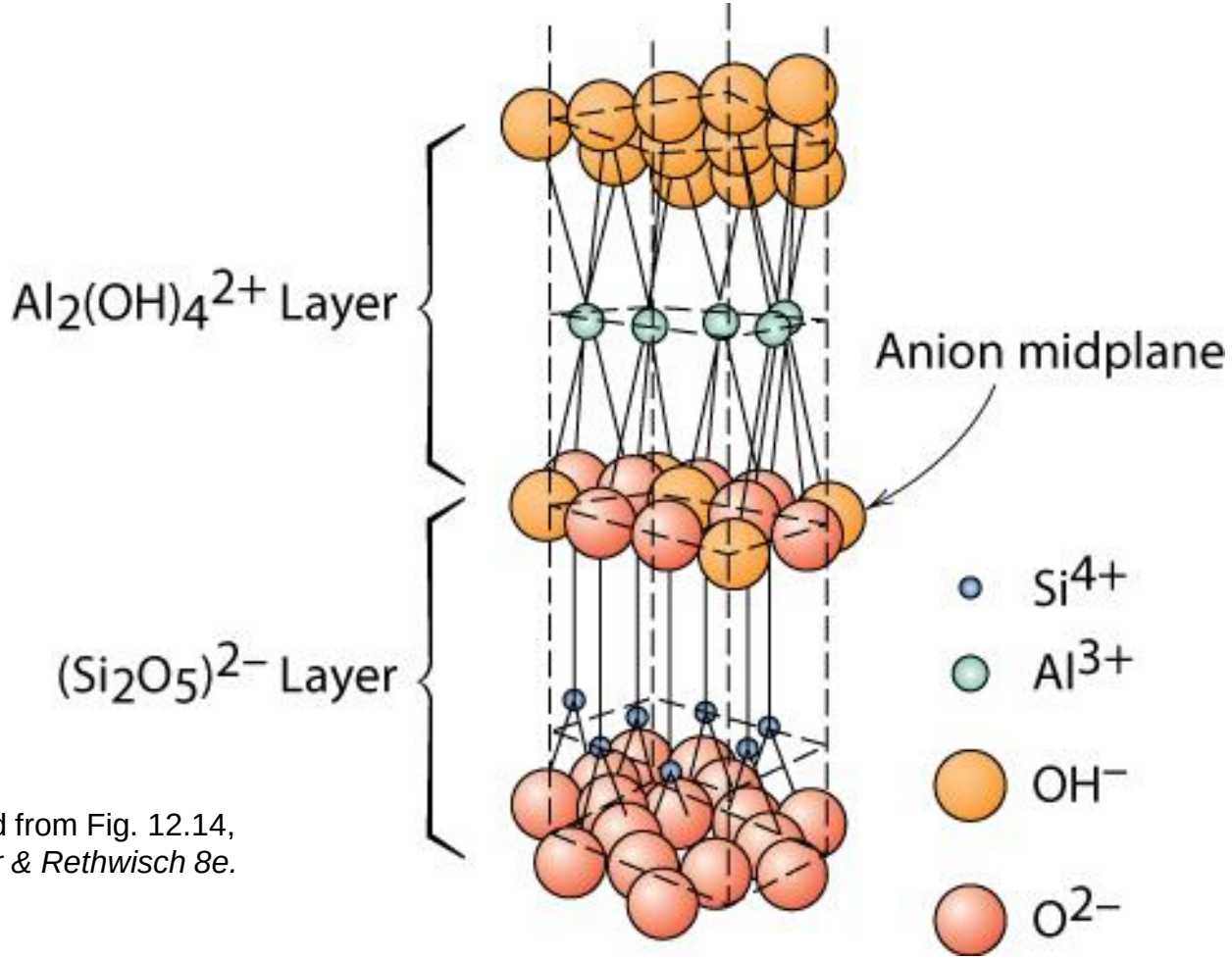
- Negative charge balanced by adjacent plane rich in positively charged cations



Adapted from Fig. 12.13, *Callister & Rethwisch 8e.*

Layered Silicates (cont.)

- Kaolinite clay alternates $(Si_2O_5)^{2-}$ layer with $Al_2(OH)_4^{2+}$ layer



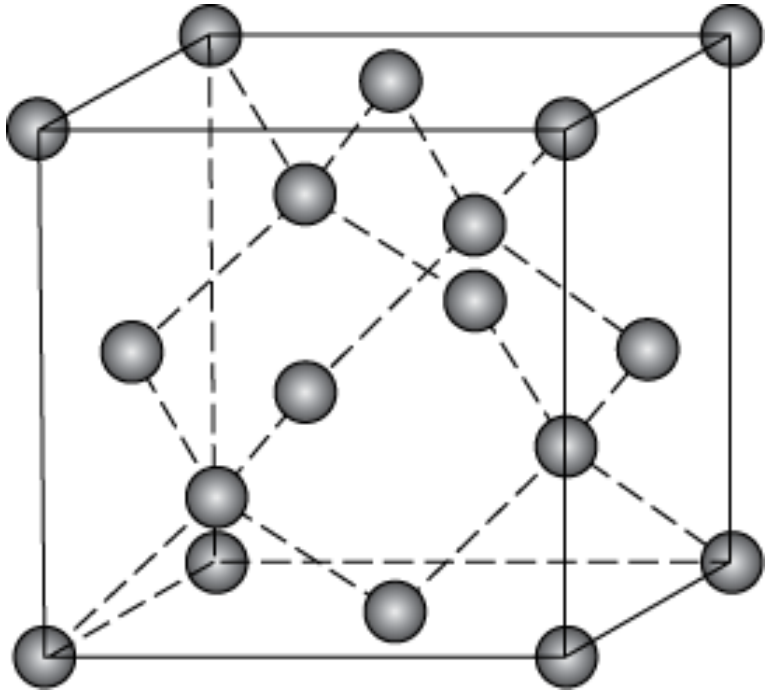
Adapted from Fig. 12.14, *Callister & Rethwisch 8e.*

Note: Adjacent sheets of this type are loosely bound to one another by van der Waal's forces.

Polymorphic Forms of Carbon

(1) **Diamond**

- Tetrahedral bonding of carbon atoms
  - 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.

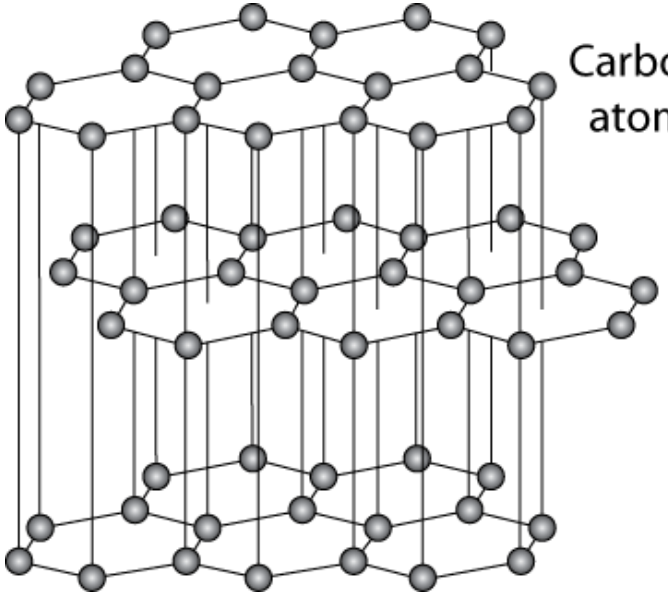


Adapted from Fig. 12.15,
Callister & Rethwisch 8e.

Polymorphic Forms of Carbon (cont)

(2) **Graphite**

– Layered structure – parallel hexagonal arrays of carbon atoms



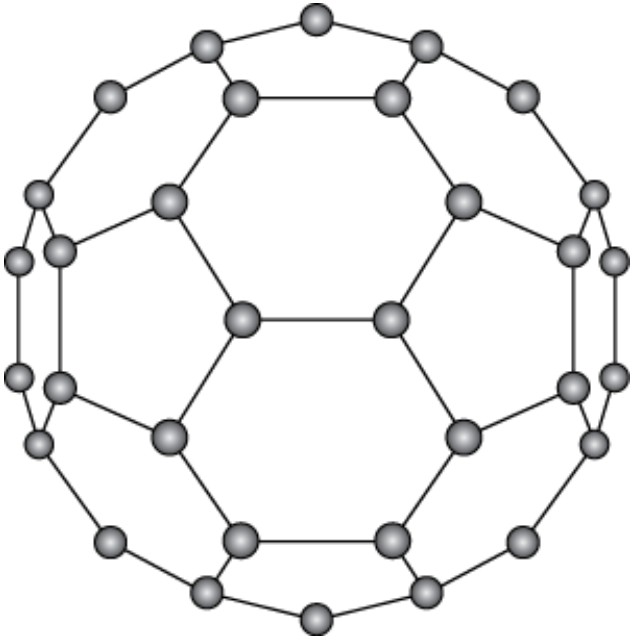
Adapted from Fig. 12.17, *Callister & Rethwisch 8e.*

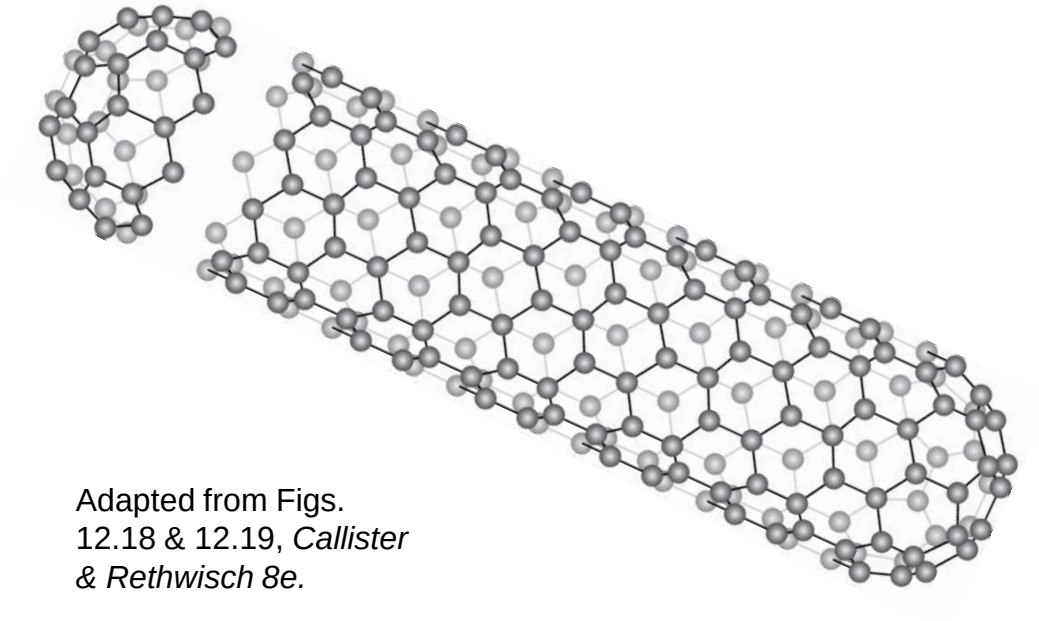
– Weak secondary bonding (van der Waal's forces) between layers → planes slide easily over one another – as good lubricant

Polymorphic Forms of Carbon (cont)
Fullerenes and Nanotubes

Others

- Fullerenes – spherical cluster of 60 carbon atoms, C_{60}
  - Like a soccer ball
- Carbon nanotubes – sheet of graphite rolled into a tube
  - Ends capped with fullerene hemispheres



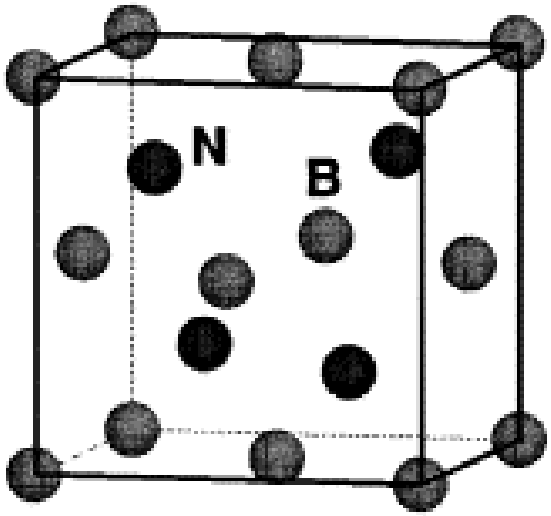


Adapted from Figs. 12.18 & 12.19, *Callister & Rethwisch 8e.*

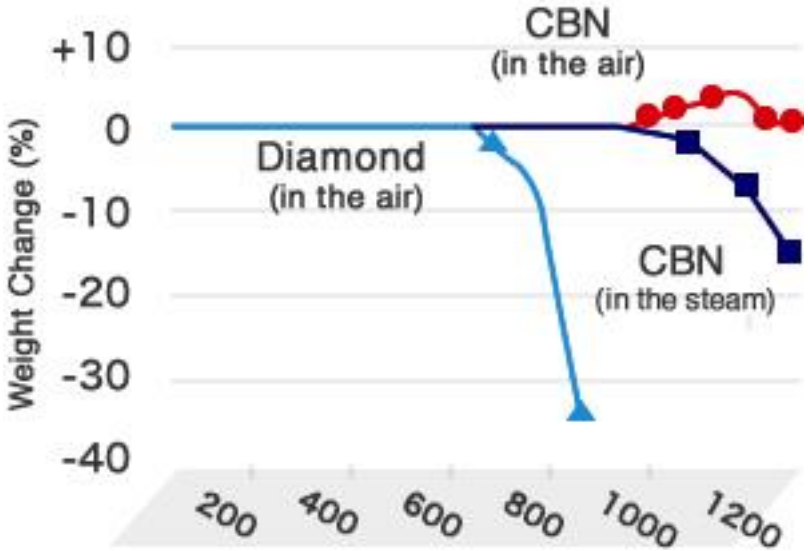
Boron Nitride: Cubic vs. Hexagonal

Cubic BN (*c*BN)

All covalent bonding

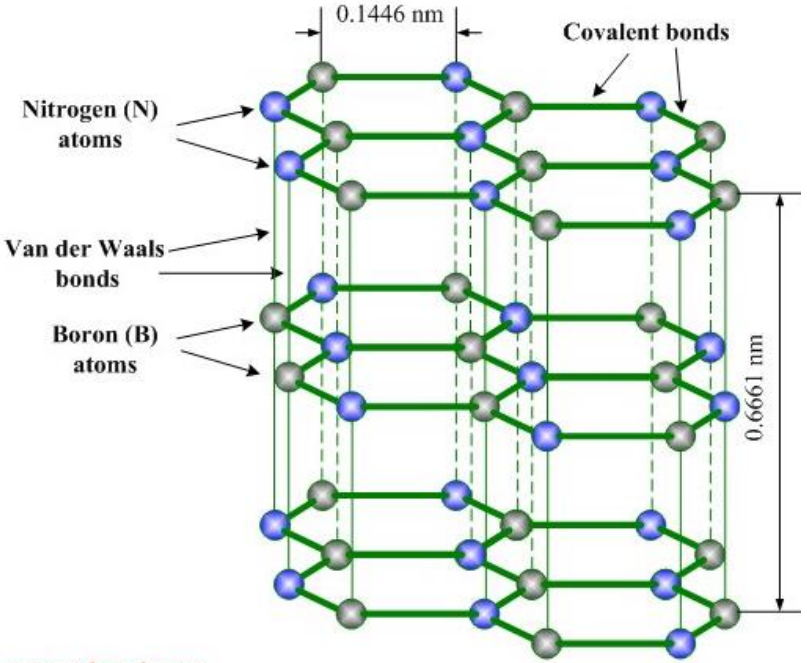


http://www.sciencedirect.com/science/article/pii/S0925963502003291



Hexagonal BN (*h*BN):

secondary bonding between layers



*c*BN is extremely hard (second only to diamond) and useful for machining cast iron, while *h*BN is extremely soft and useful as a lubricant

http://www.asahidia.co.jp/eng/support/alphabet/