

Introduction to Engineering Materials
Metal and Ceramic Structures

Part 2

Ionic crystals, silica, silicates, and carbon

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Ionic Crystals

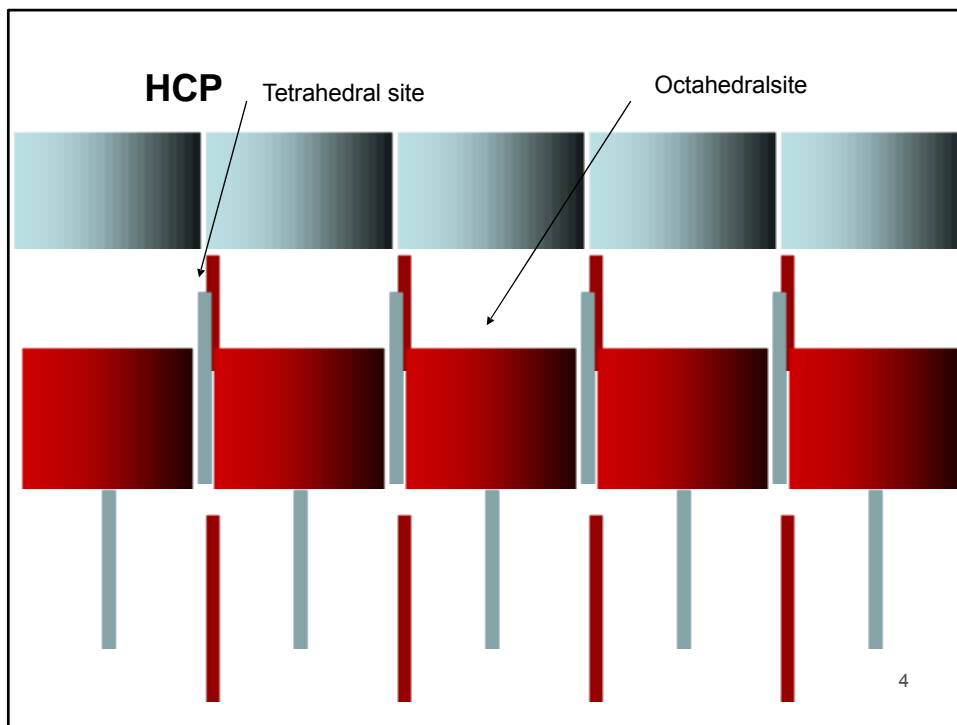
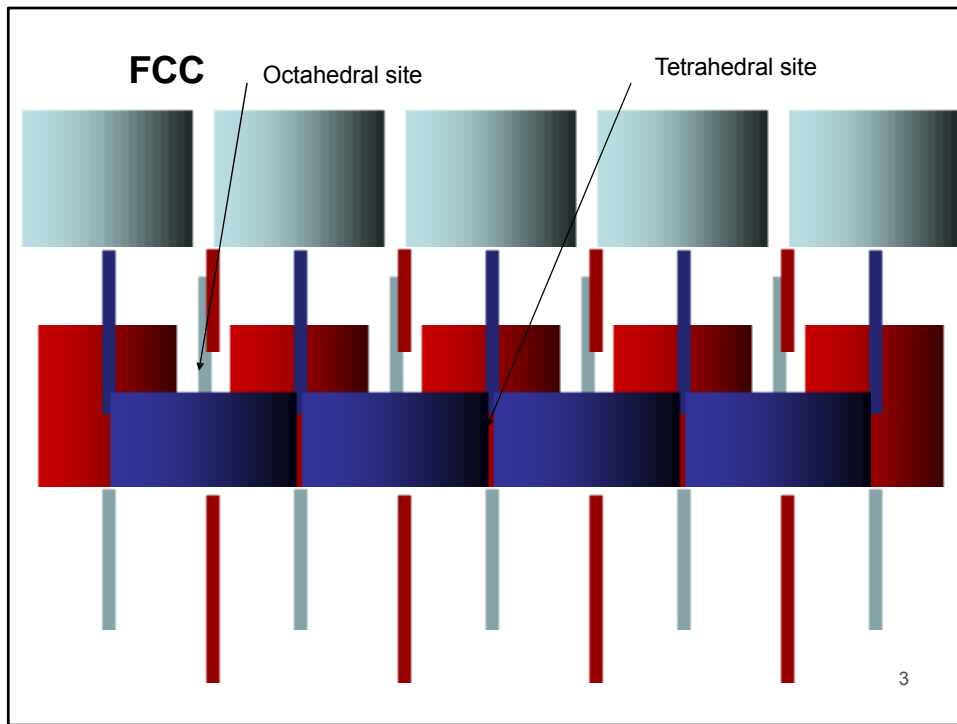
Table 12.1 For Several Ceramic Materials, Percent Ionic Character of the Interatomic Bonds

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

Note: larger anion radius

Most ionic crystals can be considered as close-packed structure of anions with cations in the interstitial sites.

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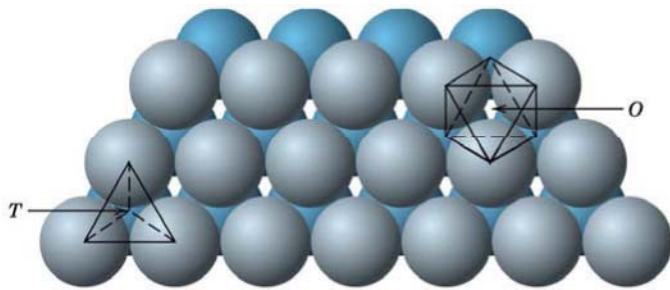
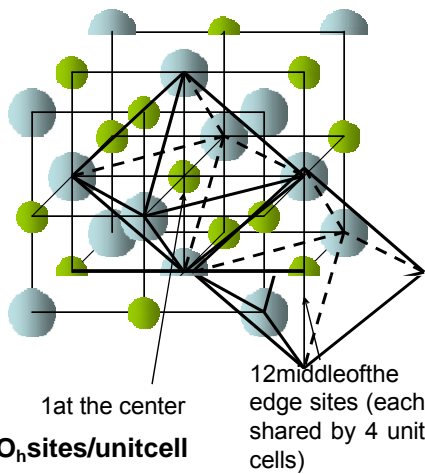


FIGURE 12.7 The stacking of one plane of close-packed spheres (anions) on top of another; tetrahedral and octahedral positions between the planes are designated by *T* and *O*, respectively. (From W. G. Moffatt, G. W. Pearsall, and J. Wulff, *The Structure and Properties of Materials*, Vol. 1, *Structure*. Copyright © 1964 by John Wiley & Sons, New York. Reprinted by permission of John Wiley & Sons, Inc.)

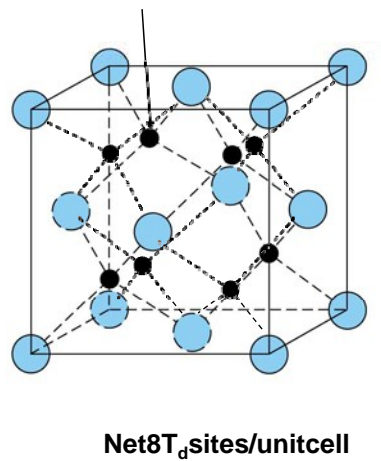
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Interstitial sites in FCC

Octahedral (O_h) sites

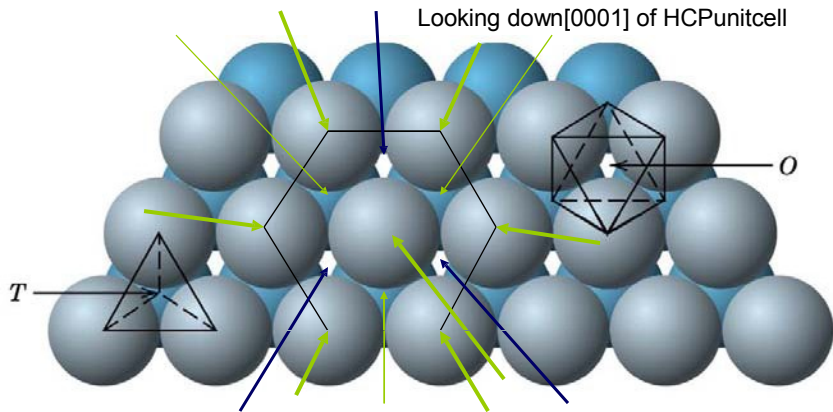


Tetrahedral (T_d) sites



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Interstitial sites in HCP



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

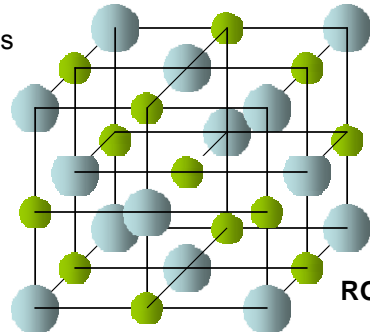
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Ionic Crystals

Many ceramic structures (ionic crystals) can be considered as close packed anions with cations in the interstitial sites.
 Recall FCC crystal...

Interstitial sites?

Octahedral sites



ROCK SALT STRUCTURE

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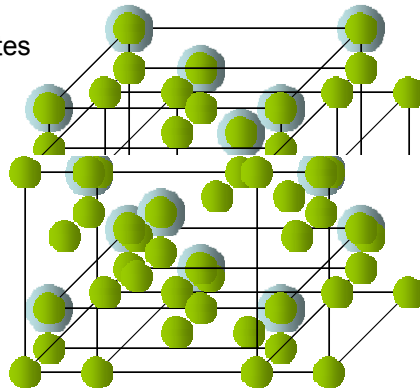
Ionic Crystals

Many ceramic structures (ionic crystals) can be considered as close-packed anions with cations in the interstitial sites.

Recall FCC crystal...

Interstitial sites?

Tetrahedral sites



Note: only $\frac{1}{2}$ of Td sites filled

ZINCBLLENDE

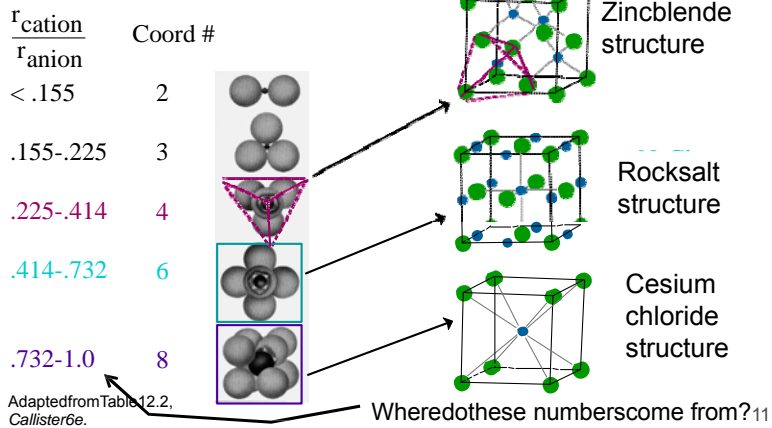
Ionic Crystals

- Charge neutrality
e.g. $\text{Ca}^{2+} \text{F}^-$ CaF_2
- Atomic Size (ratio of atomic radii).
- Stable configuration when anions surrounding a cation are all in contact with the cation.
- Coulomb attraction/repulsion (need net attraction)
 - Cations want to maximize # of neighboring anions and vice versa.

COORDINATION#ANDIONICRADII

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

How many anions can you arrange around a cation?



Cation-anion stable configuration

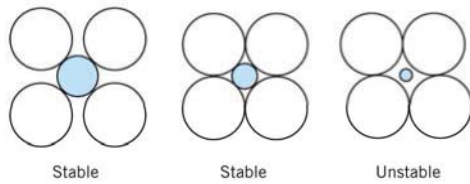
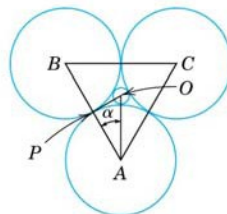
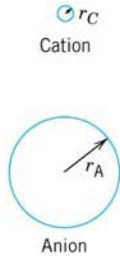


FIGURE 12.1 Stable and unstable anion-cation coordination configurations. Open circles represent anions; colored circles denote cations.

e.g. 3-coordinate



inimum ratio for 3-coordinate

$$\text{when } \cos \alpha = \frac{r_A r_A}{r_C}$$

Rewrite as

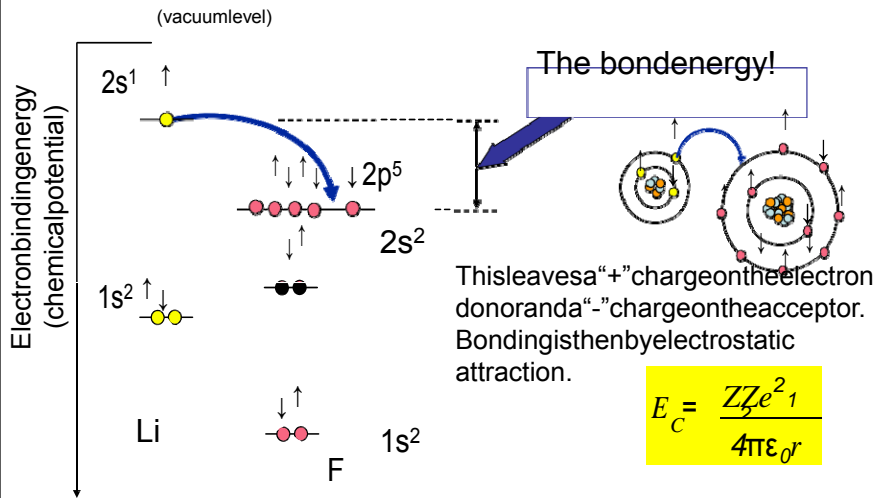
$$\frac{r_C}{r_A} = \frac{1}{\cos \alpha} - 1$$

With $\alpha = 30^\circ$

$$\frac{r_C}{r_A} = 0.155$$

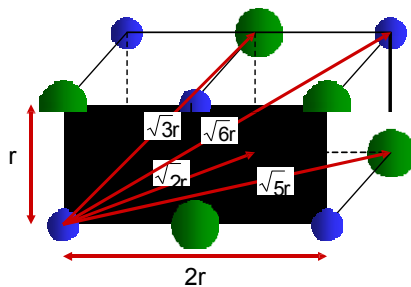
Ionic Bonds

Bonding in compounds in which there is a large difference in electronegativity. An electron is (partially) transferred from one atom to the other!



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Ideal Ionic Solid



Coulomb Energy between 2 point charges distance r apart:

	$E_C = \frac{Z_1 Z_2 e^2}{4\pi\epsilon_0 r}$
CGS	SI

$$E = -\frac{6e^2}{r} + \frac{12e^2}{\sqrt{2}r} - \frac{8e^2}{\sqrt{3}r} + \frac{6e^2}{2r} - \frac{24e^2}{\sqrt{5}r} + \frac{24e^2}{\sqrt{6}r} \dots$$

$$= -\frac{e^2}{r} \left[6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{2} + \dots \right] = -M \frac{e^2}{r}$$

Madelung Constant

(depends on crystal structure but not on atomic composition)

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Ionic Solids

- Only attractive term: crystal will collapse on itself. Real ions are not point charges!

$$E = -M \frac{e^2}{r} + B \frac{e^2}{r^n}$$

Repulsion due to overlapping outer electron density of adjacencies etc.. (B is a constant)

- At equilibrium distance r_0 , energy is at minimum:

$$\frac{dE}{dr} = M \frac{e^2}{r^2} - \frac{nBe^2}{r^{n+1}} = 0$$

$$B = \frac{M}{n} r_0^{n-1}$$

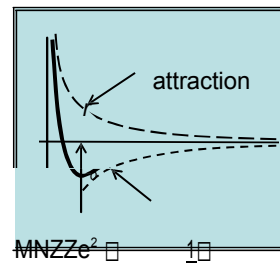
$$E_{r=r_0} = -M \frac{e^2}{r_0} + \frac{M}{n} \frac{e^2}{r_0} = -M \frac{e^2}{r_0} \left(1 - \frac{1}{n}\right)$$

$$E_{r=r_0} = - \frac{MnZe^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

- In general (molar lattice energy):

$$U = - \frac{MnZe^2}{4\pi\epsilon_0 r_0} \left(1 - \frac{1}{n}\right)$$

E repulsion



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Example Problem: Ionic Solids

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

	r_0	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_0) correspond to larger lattice energies (i.e. $U \propto \frac{1}{r_0}$).

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.

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AX type crystals

NaCl: cation radius = 0.102 nm
 anion radius = 0.181 nm
 RATIO = 0.564

What coordination number do we expect?

Charge neutrality (1:1 cation to anion ratio)

What is the resulting crystal structure?

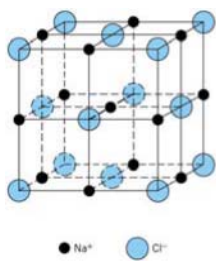


FIGURE 12.2 A unit cell for the rock salt, or sodium chloride (NaCl), crystal structure.

ROCK SALT STRUCTURE

(other solids with rock salt structure: MgO, MnS, LiF, FeO...)

Coordination Number	Cation-Anion Radius Ratio	Coordination Geometry
2	< 0.155	
3	0.155-0.225	
4	0.225-0.414	
6	0.414-0.732	
8	0.732-1.0	

AX type crystals

ZnS: cation radius = 0.074 nm
 anion radius = 0.184 nm
 RATIO = 0.402

Expect coordination # = 4

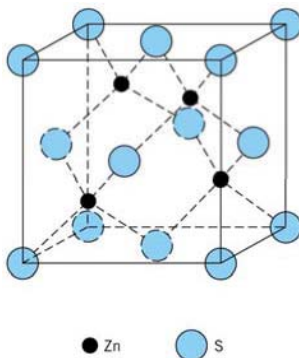


FIGURE 12.4 A unit cell for the zinc blende (ZnS) crystal structure.

Zincblende structure

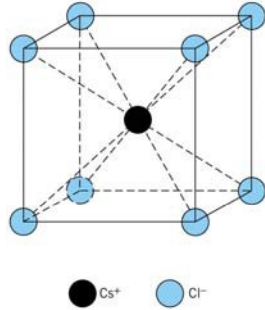
(other solids with zinc blende structure: ZnTe, CdS, SiC...)

AX type crystals

CsCl: cation radius = 0.170 nm
 anion radius = 0.181 nm
 RATIO = 0.939

Expect coordination # = 8

FIGURE 12.3 A unit cell for the cesium chloride (CsCl) crystal structure.



CsCl structure

Similar to considering NaCl as FCC of Cl⁻ with Na⁺ in Octahedral sites, CsCl can be considered as simple cubic lattice of Cl⁻ with Cs⁺ in all interstitial sites...

Note: this is similar but is not BCC.

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A_mX_p type (m and/or p ≠ 1)

CaF₂ (Fluorite) $\frac{r_{\text{cation}}}{r_{\text{anion}}} = \frac{0.100}{0.133} \approx 0.8$ → Coord. # = 8

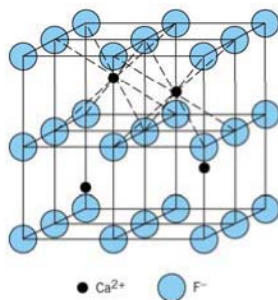
CsCl structure for 8-coordinated system... but that leads to 1:1 cation:anion.

Here, there are twice as many anions as cations.

Coordination # for anions is 4!

What should the structure look like?

FIGURE 12.5 A unit cell for the fluorite (CaF₂) crystal structure.



One cation in every other simple cubic "unit cell" of anions.

Other crystals with fluorite structure: UO₂, ThO₂...

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$A_m B_n X_p$ Type

1. ABX_3 Type (e.g. Barium titanate $BaTiO_3$) Perovskite structure

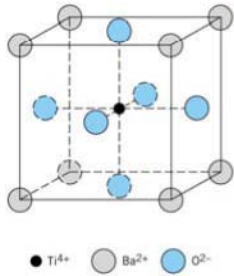


FIGURE 12.6 A unit cell for the perovskite crystal structure.

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

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

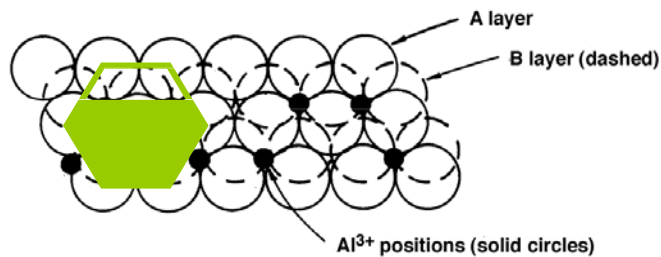
- FCC of O^{2-}
- Mg^{2+} in tetrahedral sites (1/8 filled)
- Al^{3+} in octahedral sites (half filled)

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Example

Corundum structure of Al_2O_3 consists of O^{2-} ions in HCP arrangement with Al^{3+} ions occupying octahedral sites.

1. What fraction of octahedral sites are filled?
2. Sketch 2 O^{2-} planes with Al^{3+} ions.



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Crystal 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

In general:

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

Example: Calculated density of NaCl.

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Silica & Silicates

Primarily composed of Si and O

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

Charge neutrality: $\text{Si}^{4+} : \text{O}^{2-} = 1:2 \rightarrow \text{SiO}_2$

However:

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

What structure(s) do we expect?

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		
Tl ⁺	0.061		

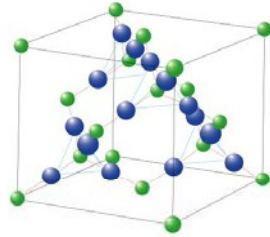
Tetrahedral Silica unit



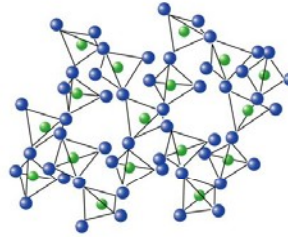
Crystalline Silica

Crystalline silica

Cristobalite, SiO_2



Quartz



Each O atom is shared by two tetrahedral units

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Crystalline & non-crystalline silica

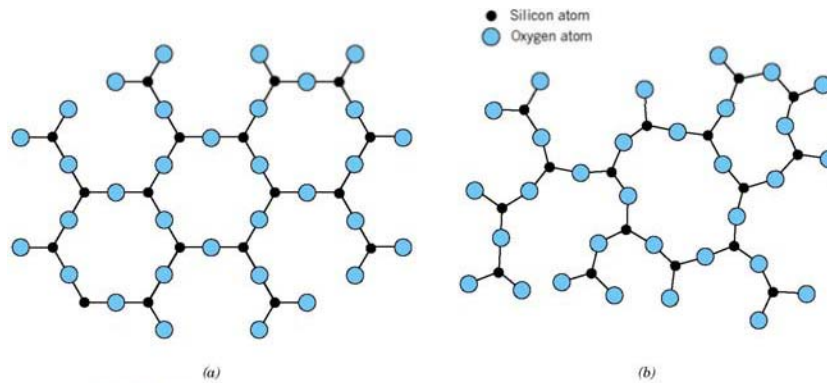


FIGURE 3.18 Two-dimensional schemes of the structure of (a) crystalline silicon dioxide and (b) noncrystalline silicon dioxide.

Note, relatively open structure but large bond strength
 (e.g. quartz: density = 2.65 g/cm^3 , mp = 1710°C) Non-crystalline form: fused silica or vitreous silica

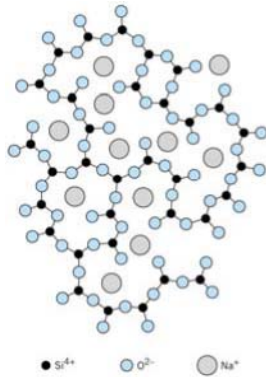
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Silicate glasses

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

Silicates: amorphous silica with impurities

FIGURE 12.11 Schematic representation of ion positions in a sodium-silicate glass.



Sodium-silicate glass

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Silicate glasses

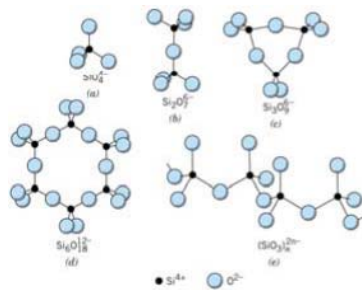


FIGURE 12.12 Five silicate ion structures formed from SiO_4^{4-} tetrahedra.

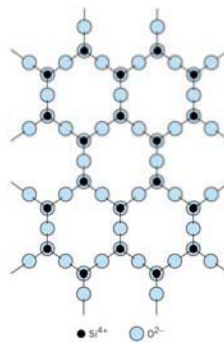
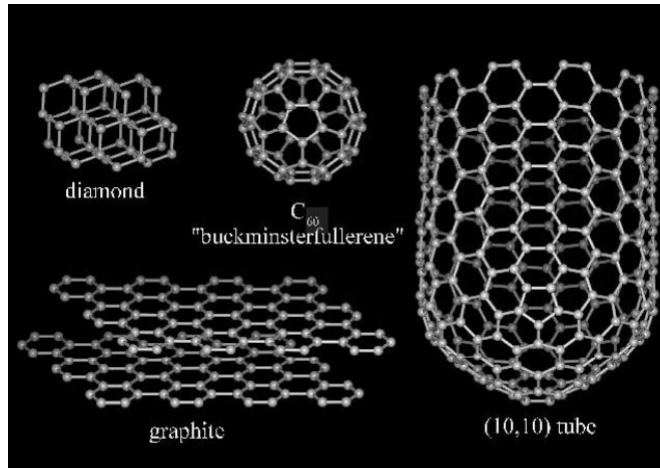


FIGURE 12.13 Schematic representation of the two-dimensional silicate sheet structure having a repeat unit formula of $(\text{Si}_2\text{O}_5)^{2-}$.

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Carbon



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

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Diamond

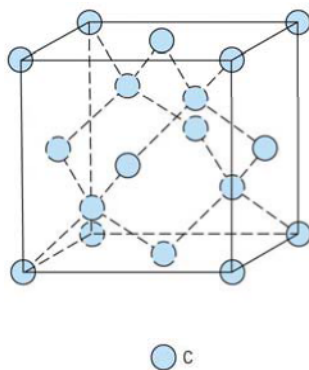


FIGURE 12.15 A unit cell for the diamond cubic crystal structure.

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

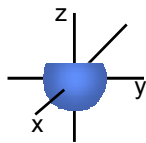


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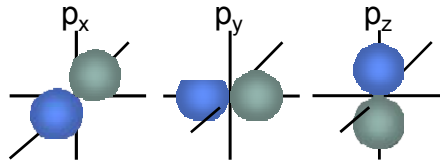
Recall hybridization:

Atomic Orbitals

s-orbital

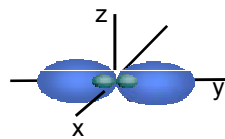


the three orbitals

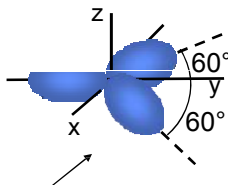


Hybridization

1x s + 1x p = sp-orbitals

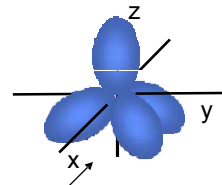


1x s + 2x p = sp²-orbitals



Hybridization for graphitic carbon

1x s + 3x p = sp³-orbitals



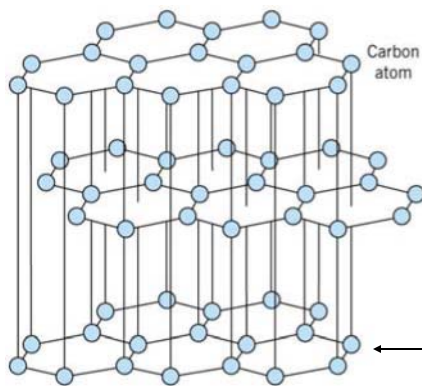
Hybridization for Diamond

What are the hybridizations for graphite and diamond?

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Graphite

FIGURE 12.17 The structure of graphite.



Graphene: single atomic sheet of graphitic carbon

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Fullerenes&Nanotubes

FIGURE 12.18 The structure of a C_{60} molecule.

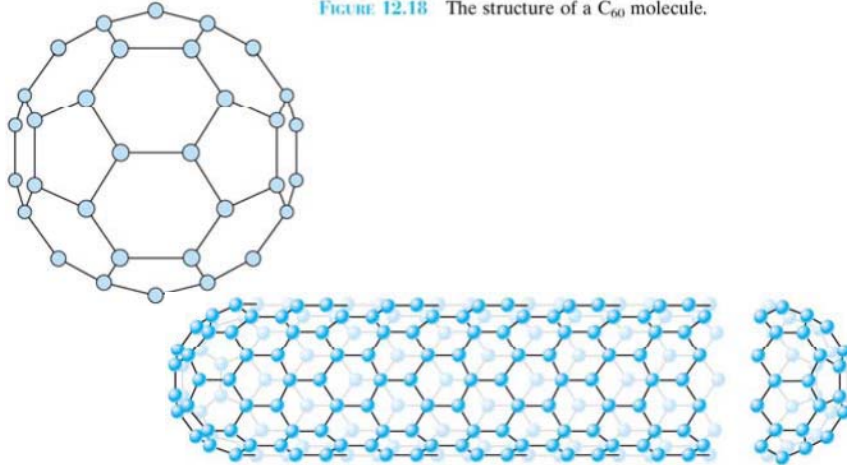
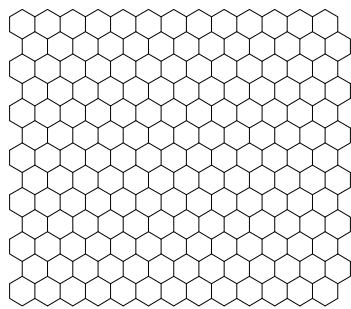


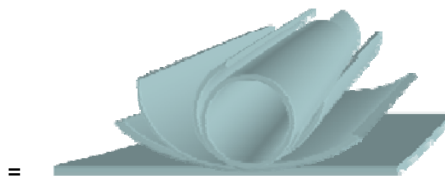
FIGURE 12.19 The structure of a carbon nanotube. (Reprinted by permission from *American Scientist*, magazine of Sigma Xi, The Scientific Research Society. Illustration by Aaron Cox/*American Scientist*.)

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CarbonNanotubes



graphene



Carbonnanotube="rolledup"graphene



Single-WalledCarbonnanotube
~<0.7-5 nm diameter



Multi-WalledCarbonnanotube
>2 nmdiameter(canbe
largerthan 100nm)

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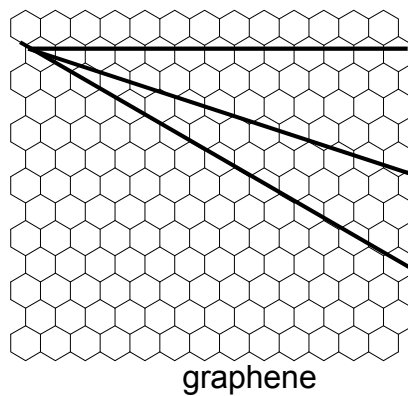
Carbon Nanotubes

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

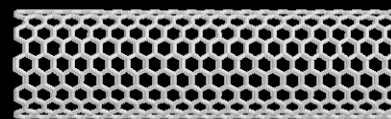


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Carbon nanotubes



graphene



(10,10) SWNT
ARMCHAIR
Metallic

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Concepts to remember...

- Ionic crystals:
 - Interstitial sites
 - Ionic radii ratios
 - Different structures
 - Lattice energy
- Silica & silicates.
- Carbon (diamond, graphite, fullerenes).

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