

# Chem 241

## Lecture 20



# Announcement

March 26 → Second Exam

## Recap

Ellingham Diagram

Inorganic Solids

Unit Cell

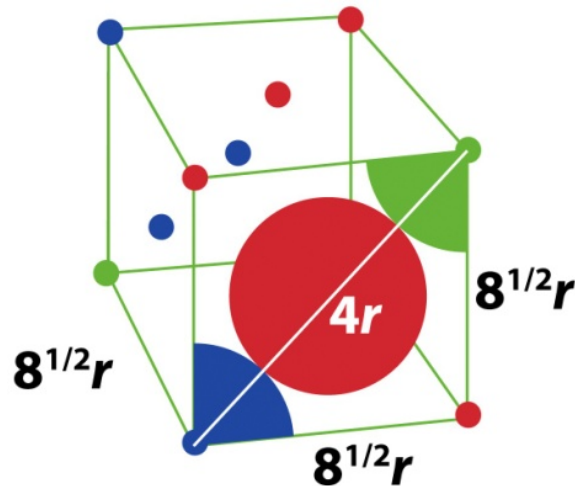
Fractional Coordinates

Packing



# Inorganic Solids

- Atoms entirely within the unit cell (such as the center of a bcc cell) count as one atom.
- Atoms centered in the face of a unit cell (such as the faces in an fcc cell) count as one-half atom.
- Atoms on an edge of the unit cell count as one-quarter atom.
- Atoms at the corners of a cubic, tetragonal, or orthorhombic cell count as one-eighth of an atom.

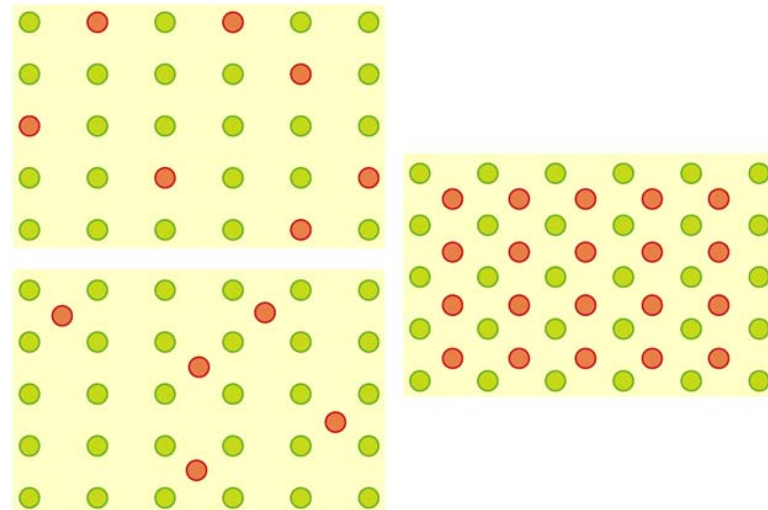
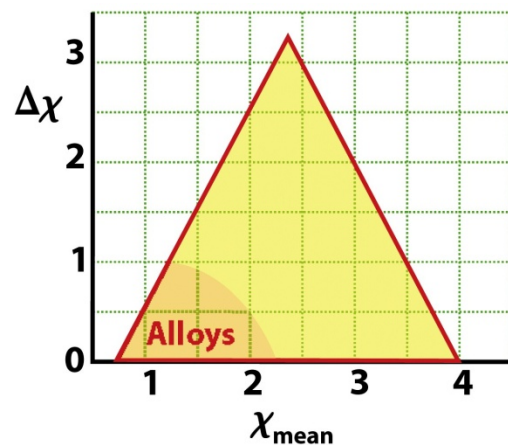


26% of the volume of a close packed structure is space.

# Inorganic Solids

An **alloy** is a blend of metallic elements prepared by mixing the molten components and cooling to produce a solid that has metallic properties.

- Typically form between electropositive metals that have similar electronegativities.
- Solid solutions may be substitutional or interstitial.



# Substitutional Solid Solutions

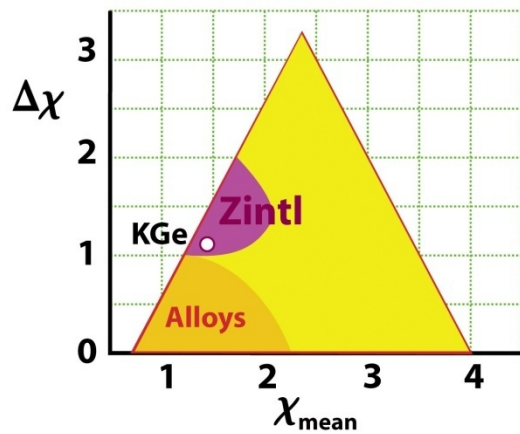
Substitutional solid solutions typically form when:

1. The metals have similar size; the Atomic radii of the elements is within  $\sim 15\%$
2. The crystal structures of the pure metals are the same
3. Electronegativity is similar.

# Interstitial Solid Solutions

- Formed between metals and smaller atoms (that fit in the holes).
- They can be stoichiometric substances like WC or randomly distributed non-stoichiometric compounds.
- Holes determine what can go in the open spaces

# Intermetallic compounds



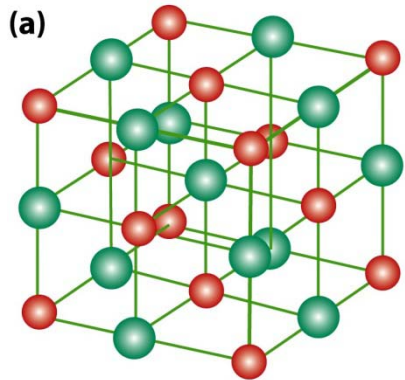
- When liquid mixtures cool, they sometimes form phases of stoichiometric composition with definite structures.
- Examples include  $\text{MgZn}_2$ ,  $\text{Cu}_3\text{Au}$ ,  $\text{Na}_5\text{Zn}_{21}$  etc.
- Often involve elements with a difference in electronegativity (Zintl phases).
- They are in the gray area between metals and ionic solids. They are brittle like ionic materials, but have a luster like metals.

# Ionic solids

- Many ionic solids adopt one of several prototypical lattices.
- These lattices can be viewed as having a close-packed structure (ccp or hcp) in one ion, usually the largest, with the smaller ion occupying Oh or Td holes.
- Repulsions between ions of the same charge, generally expand the lattice from a close packed arrangement

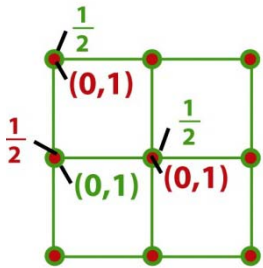


# Rock Salt

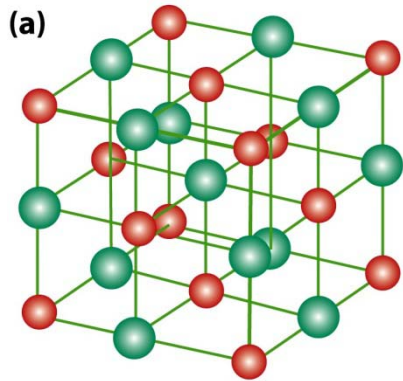


NaCl

- Can be viewed as ccp in  $\text{Na}^+$  with  $\text{Cl}^-$  in all the Oh holes.
- Has 6,6-coordination; the cation and anion have 6 nearest neighbors, respectively.
- Visualize the lattice:
  - The  $\text{Cl}^-$  in the center is entirely within the unit cell = 1
  - It has 6 nearest neighbors, all  $\text{Na}^+$  (first coordination sphere) that occupy faces,  $(6/2) = 3$
  - It has 12  $\text{Cl}^-$  in the second coordination sphere that occupy edges,  $12/4 = 3$
  - It has 8  $\text{Na}^+$  in the third coordination sphere that occupy corners,  $8/8 = 1$
  - There are 4  $\text{Cl}^-$  in the unit cell (ccp) and 4  $\text{Na}^+$ , the stoichiometry is 1:1, formula unit = NaCl and  $Z = 4$

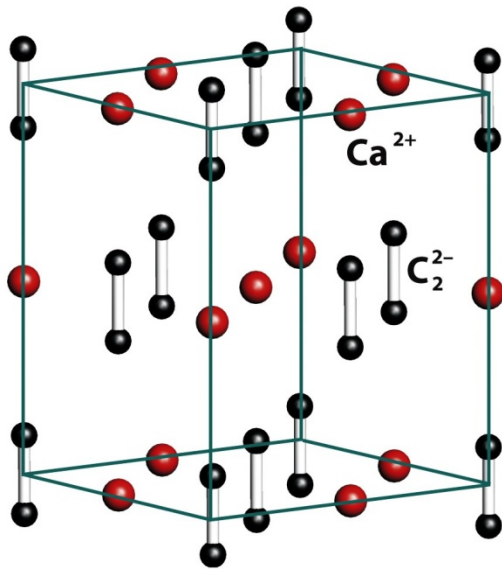


# Rock Salt



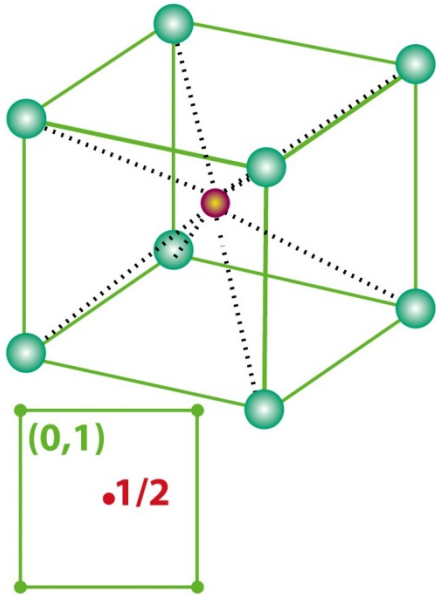
KBr, AgCl, AgBr, CaO, FeO, SnAs

Many other 1:1 compounds share this structure  $\rightarrow$   $[\text{Co}(\text{NH}_3)_3][\text{TiCl}_6]$



$\text{CaC}_2$ , CsO, KCN,  $\text{FeS}_2$

# CsCl Structure



Similar to the bcc lattice adopted by W, **not** close-packed

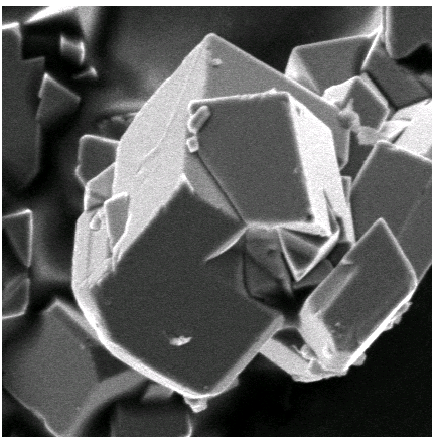
Primitive structure with alternative atom in the hole

Can be viewed as interlocking cubic cells of Cs<sup>+</sup> and of Cl<sup>-</sup>.

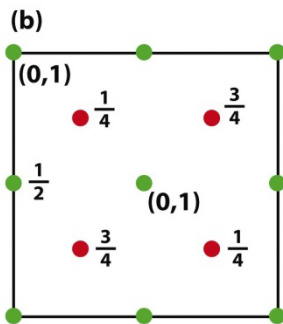
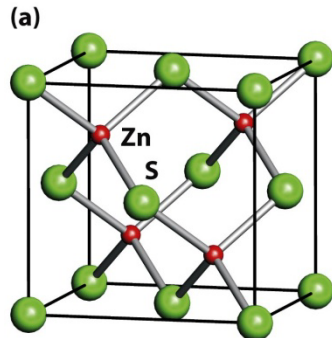
There are 8 Cl<sup>-</sup> ions at corners of the cubic unit cell  
 $8/8 = 1$  Cl<sup>-</sup> per unit cell

There is one Cs<sup>+</sup> in the center, coordinated to the 8 Cl<sup>-</sup>  
Formula unit = CsCl, stoichiometry is 1:1,  $Z = 1$ .

8,8-coordination

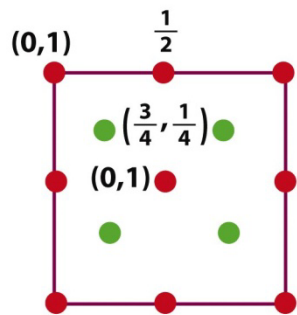
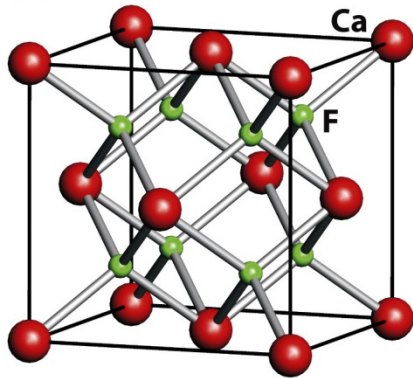


# ZnS



- Sphalerite/ Zinc-blende
- Can be viewed as ccp in  $S^{2-}$  with  $Zn^{2+}$  in half the Td holes.
- Since all the Td holes are completely contained within a single unit cell, all 4 Zn ions count in the unit cell
- There are two types of S anions, those in faces,  $6/2 = 3$
- And those in corners,  $8/8 = 1$ .
- The stoichiometry is 1:1;  $Z = 4$
- 4,4-coordination

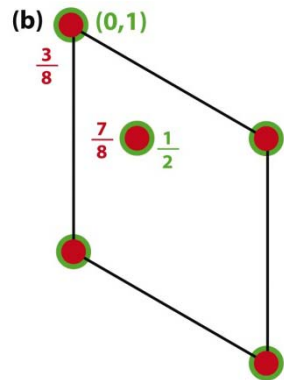
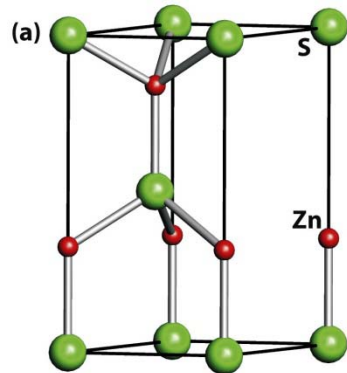
# Fluorite Structure



- Can be viewed as ccp in one ion with the other in all the  $T_d$  holes. In the case of fluorite, this would be ccp in  $\text{Ca}^{2+}$  with  $\text{F}^-$  in all the  $T_d$  holes. (Note anions not close packed, cations are.)
- Since there are twice as many  $T_d$  holes in a close packed lattice (8) than there are spheres (4), the stoichiometry is 1:2.
- The formula unit is  $\text{CaF}_2$   $Z = 4$ .
- 8,4-coordination.
- In anti-fluorite, the positions of the cations and anions are reversed. *E.g.*,  $\text{Li}_2\text{O}$ . Here the lattice is ccp in  $\text{O}^{2-}$  with  $\text{Li}^+$  in all the  $T_d$  holes.
- 4,8-coordination

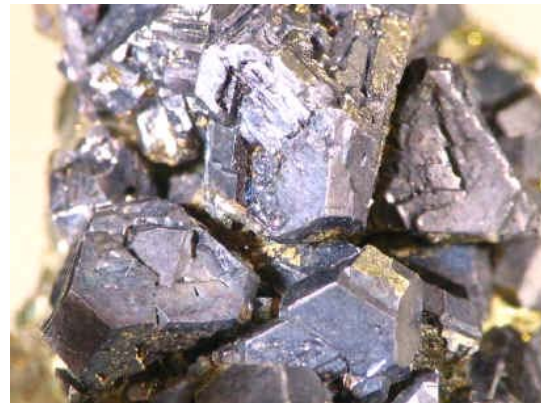


# Wurtzite

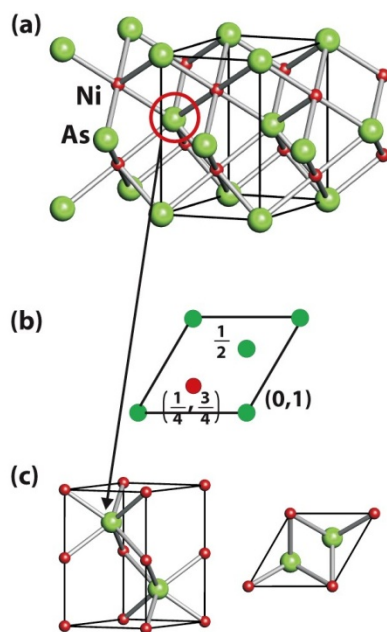


Wurtzite (another polymorph of ZnS)

- Can be viewed as hcp in  $S^{2-}$  with  $Zn^{2+}$  in  $\frac{1}{2}$  the Td holes.
- Stoichiometry = 1:1
- Formula unit ZnS,  $Z = 2$
- 4,4-coordination



# Nickel Arsenide



- Can be viewed as expanded hcp in  $\text{As}^{2-}$  with  $\text{Ni}^{2+}$  in  $\text{O}_h$  holes.
- Stoichiometry = 1:1
- Formula unit =  $\text{NiAs}$ ,  $Z = 2$
- 6,6-coordination
- As sites are trigonal prismatic, not  $\text{O}_h$
- Often preferred by MX compounds with p ions.
- The possible M-M bonding between atoms in adjacent layers, and is thus common for alloys where the metals interact.

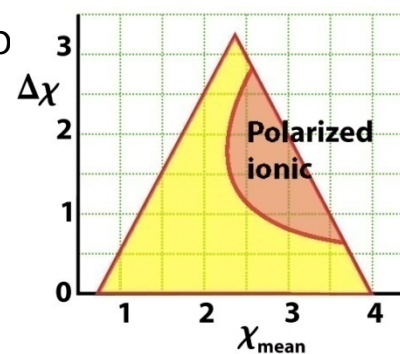
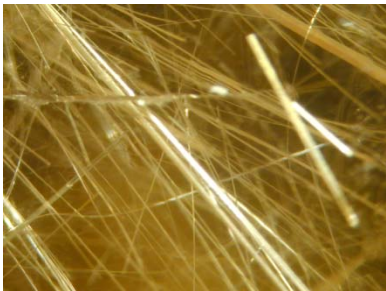
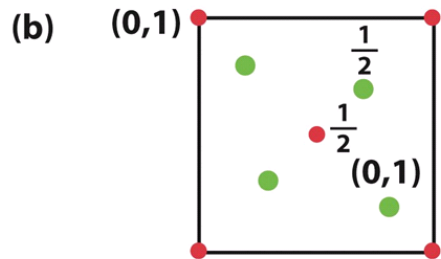
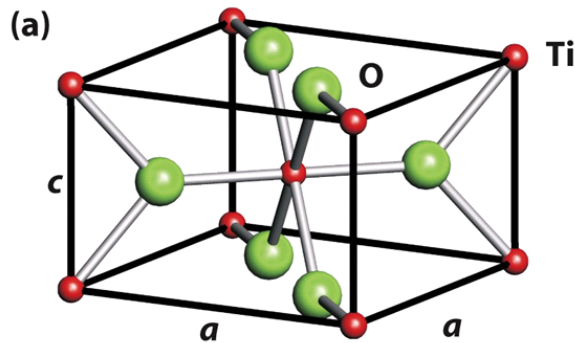


Figure 3-36  
Shriver & Atkins Inorganic Chemistry, Fourth Edition  
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# Rutile



( $\text{TiO}_2$ )

- Can be viewed as expanded hcp in  $\text{Ti}^{4+}$  with  $\text{O}^{2-}$  in  $\frac{1}{2}$  Oh holes
- Very distorted by tendency of  $\text{Ti(IV)}$  to adopt Oh geometry.
- Each  $\text{Ti}^{4+}$  is 6-coordinate, thus each  $\text{O}^{2-}$  is 3-coordinate, *i.e.*, 6,3-coordination.
- Stoichiometry is 1:2
- Formula unit is  $\text{TiO}_2$ ,  $Z = 2$



# Inorganic solids

**Table 3.4** The crystals structures of compounds

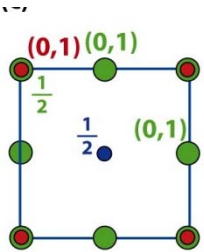
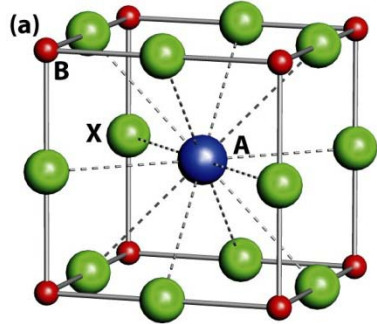
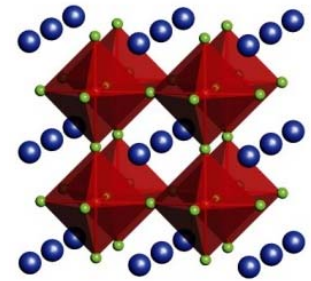
Crystal structure	Example*
Antifluorite	$K_2O$ , $K_2S$ , $Li_2O$ , $Na_2O$ , $Na_2Se$ , $Na_2S$
Caesium chloride	<b>CsCl</b> , $CaS$ , $TlSb$ , $CsCN$ , $CuZn$
Fluorite	<b>CaF<sub>2</sub></b> , $UO_2$ , $BaCl_2$ , $HgF_2$ , $PbO_2$
Nickel arsenide	<b>NiAs</b> , $NiS$ , $FeS$ , $PtSn$ , $CoS$
Perovskite	<b>CaTiO<sub>3</sub></b> , $SrTiO_3$ , $PbZrO_3$ , $LaFeO_3$ , $LiSrH_3$ , $KMnF_3$
Rock salt	<b>NaCl</b> , $KBr$ , $RbI$ , $AgCl$ , $AgBr$ , $MgO$ , $CaO$ , $TiO$ , $FeO$ , $NiO$ , $SnAs$ , $UC$ , $ScN$
Rutile	<b>TiO<sub>2</sub></b> , $MnO_2$ , $SnO_2$ , $WO_2$ , $MgF_2$ , $NiF_2$
Sphalerite (zinc blende)	<b>ZnS</b> , $CuCl$ , $CdS$ , $HgS$ , $GaP$ , $InAs$
Spinel	<b>MgAl<sub>2</sub>O<sub>4</sub></b> , $ZnFe_2O_4$ , $ZnCr_2S_4$
Wurtzite	<b>ZnS</b> , $ZnO$ , $BeO$ , $MnS$ , $AgI$ , $AlN$ , $SiC$ , $NH_4F$

\* The substance in bold type is the one that gives its name to the structure.

**Table 3.5** The relation of structure to the filling of holes

Close-packing type	Hole filling	Structure type (exemplar)
Cubic (ccp)	All octahedral	Rock salt (NaCl)
	All tetrahedral	Fluorite (CaF <sub>2</sub> )
	Half tetrahedral	Sphalerite (ZnS)
Hexagonal (hcp)	All octahedral	Nickel arsenide (NiAs); with some distortion from perfect hcp
	Half octahedral	Rutile (TiO <sub>2</sub> ); with some distortion from perfect hcp
	All tetrahedral	No structure exists: tetrahedral holes share faces
	Half tetrahedral	Wurtzite (ZnS)

# Perovskite, $A_aB_bX_n$

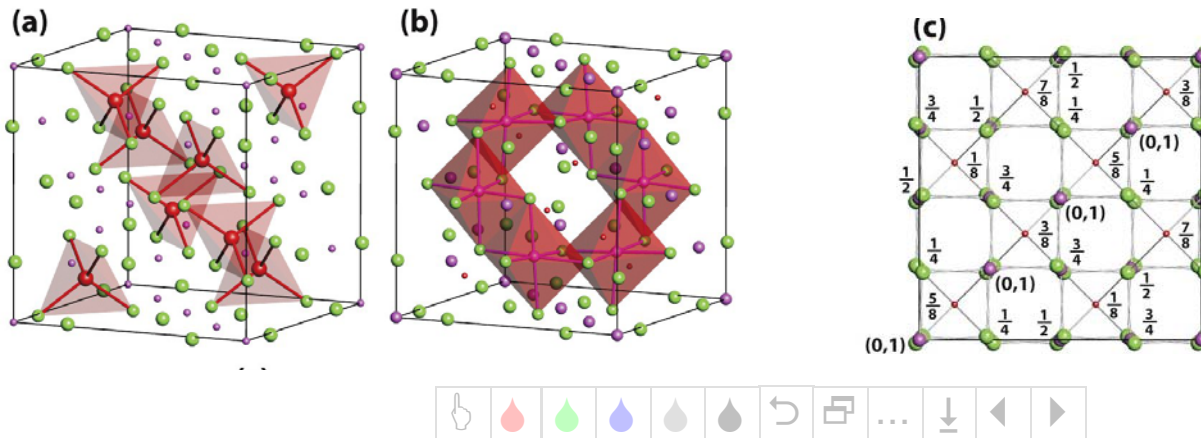


## $\text{CaTiO}_3$ , $\text{ABX}_3$

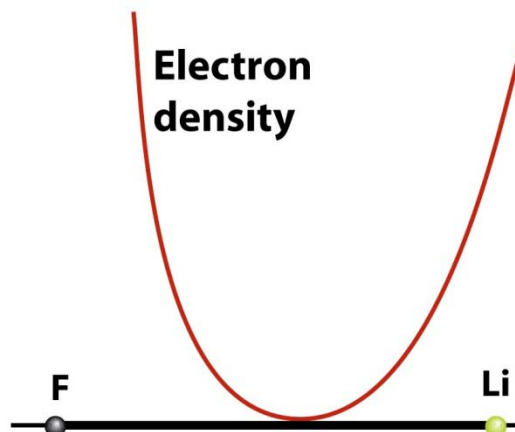
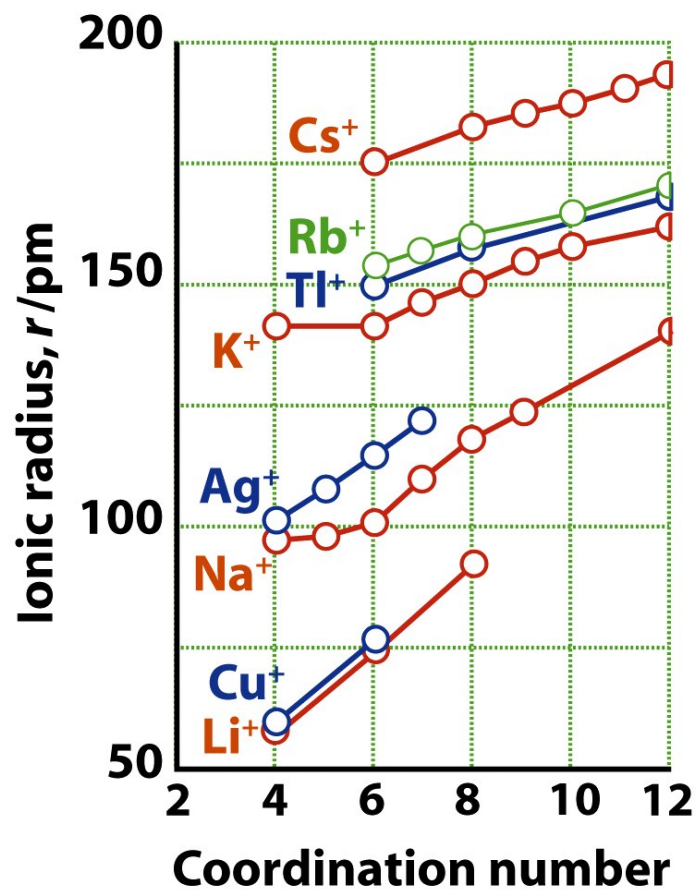
- Idealized as a cube of B cations (1 per unit cell surrounding an A cation completely contained in the center of the unit cell, with X atoms located in the  $O_h$  holes on the cube edges ( $12/4 = 3$ ).
- Usually A is large and has a small charge, B is small and has a large charge.
- The sum of the charges on the cations must = the sum of the charges on the anions, in this case 6.  
 e.g., for perovskite  $\text{Ca(II)} + \text{Ti(IV)}$ . But could be (III) and (III), or even mixed, as in  $\text{La}(\text{Ni}_{0.5}\text{Ir}_{0.5})\text{O}_3$ .
- Often have interesting electrical properties

# Spinel

- $\text{MgAl}_2\text{O}_4$ ,  $\text{AB}_2\text{X}_4$ 
  - Viewed as ccp array of  $\text{O}^{2-}$  ions with A occupying 1/8 of  $\text{T}_d$  holes and B occupying 1/2 of  $\text{O}_h$  holes.
  - Normally B is smaller and more highly charged than A
  - Inverse spinels have B atoms in the occupied  $\text{T}_d$  holes and in 1/2 the occupied  $\text{O}_h$  holes.  $\text{B}[\text{AB}]\text{O}_4$ , where brackets denote the ions in the  $\text{O}_h$  holes.
  - Sometimes A and B are the same element:
    - $\text{Fe(II)Fe(III)}_2\text{O}_4$



# Ionic Radius



**Table 1.5** Ionic radii,  $r/\text{pm}^*$

<b>Li<sup>+</sup></b> 59(4) 76(6)	<b>Be<sup>2+</sup></b> 27(4)	<b>B<sup>3+</sup></b> 11(4)			<b>N<sup>3-</sup></b> 146	<b>O<sup>2-</sup></b> 135(2) 138(4) 140(6) 142(8)	<b>F<sup>-</sup></b> 128(2) 131(4) 133(6)
<b>Na<sup>+</sup></b> 99(4) 102(6) 118(8)	<b>Mg<sup>2+</sup></b> 49(4) 72(6) 89(8)	<b>Al<sup>3+</sup></b> 39(4) 53(6)			<b>P<sup>3-</sup></b> 212	<b>S<sup>2-</sup></b> 184(6)	<b>Cl<sup>-</sup></b> 181(6)
<b>K<sup>+</sup></b> 138(6) 151(8) 159(10) 160(12)	<b>Ca<sup>2+</sup></b> 100(6) 112(8) 123(10) 134(12)	<b>Ga<sup>3+</sup></b> 62(6)			<b>As<sup>3-</sup></b> 222	<b>Se<sup>2-</sup></b> 198(6)	<b>Br<sup>-</sup></b> 196(6)
<b>Rb<sup>+</sup></b> 152(6) 160(8) 173(12)	<b>Sr<sup>2+</sup></b> 118(6) 125(8) 144(12)	<b>In<sup>3+</sup></b> 79(6) 92(8)	<b>Sn<sup>2+</sup></b> 83(6) 93(8)	<b>Sn<sup>4+</sup></b> 69(6)		<b>Te<sup>2-</sup></b> 221(6)	<b>I<sup>-</sup></b> 220(6)
<b>Cs<sup>+</sup></b> 167(6) 174(8) 188(12)	<b>Ba<sup>2+</sup></b> 149(6) 156(8) 175(12)	<b>Tl<sup>3+</sup></b> 88(6) <b>Tl<sup>+</sup></b> 164(6)					

\*Numbers in parentheses are the coordination number of the ion. For more values, see *Resource section 1*.

