Site Selection Rule 2

• Recall that for metals close-packed planes of atoms stacked on one another generate both FCC and HCP crystal structures.
• Similarly, a number of ceramic crystal structures may be considered in close-packed planes of ions as well as unit cells.
• Ordinarily, the close-packed planes are composed of the large anions, as these planes are stacked atop each other, small interstitial sites are created between them in which cations may reside:

Fig. The stacking of one close packed plane (red spheres) on top of another (blue spheres). Cations can fill tetrahedral and/or octahedral positions.

• As previously discussed in the FCC and HCP metal structures, each close packed site has one 6-coordinate octahedral site and two 4-coordinate tetrahedral sites (1 T+ site and 1 T- site):

• Likewise, in ionic structures (FCC anion lattices have ABCABC… stacking and HCP anion lattices have ABAB… stacking), each anion has two tetrahedral and one octahedral sites nearby.
Site Selection Rule 2 (continued)

• The composition of the ionic material can be determined by cation fractional occupation on these interstitial sites.
• Consider **Rocksalt** or **B1 crystal structure**, e.g. NaCl, Each Na\(^{+}\) has 6 Cl\(^{-}\) N.N. If we take a slice of the cube corner, along the \{111\} plane, the anions lie on this plane and the cations occupy the interstitial octahedral sites, since they have 6 N.N. anions.
• Furthermore, all octahedral sites are filled, since there is a single octahedral site per anion, and the ratio of anions to cations is 1:1.
• This leads to second site selection rule, which is based on **stoichiometry**, if all of one type of site is full the remainder have to go into other types of sites.
• **Example**: We know that an FCC unit cell has 4 \(O_H\) and 8 \(T_D\) sites. If for a specific ceramic each unit cell has 6 cations and the cations prefer \(O_H\) sites, then 4 will be in \(O_H\) sites and 2 will be in \(T_D\) sites.
• For NaCl, there are 4 Na\(^{1+}\) and 4Cl\(^{1-}\)/unit cell. Thus, the 4 Na cations will go in \(O_H\) sites.
• MgO and FeO also have Rocksalt structure.
• \(O^{2-}\) \(r_O = 0.140\) nm \( \frac{r_{Mg}}{r_{O}} = 0.514\)
• \(Mg^{2+}\) \(r_{Mg} = 0.072\) nm \(\therefore\) predicts that cations prefer octahedral sites.
• If charges on cations and anions are not the same, a compound can exist with the chemical formula $A_nB_m$, where $n$ and/or $m \neq 1$.

• Example: **Fluorite or C1 crystal structure**, $AB_2$ compound, calcium fluorite (CaF$_2$) prototype.

• It is important to note that the anions do not necessarily need to be in the close-packed eutactic positions →

• Ca$^{2+}$ ions are in the CCP eutactic sites (CN=8) and F$^-$ ions fill the tetrahedral sites (CN=4).

• Ca$^{2+}$ ($R_A=0.112$nm) and F$^-$ ($R_B=0.131$nm): $\rho=0.855$

\[
0.732 < \frac{R_A}{R_B} < 4.44
\]

• All of the tetrahedral sites ($T_D$) will be occupied because the ratio of Ca$^{2+}$ to F$^-$ is 1:2 and there are 2 $T_D$ sites per Ca$^{2+}$ (e.g., 4 Ca$^{2+} = 8$ $T_D$ sites).

• Other examples are UO$_2$, SrCl$_2$, c-ZrO$_2$, CeO$_2$

• Antifluorite structure – cations and anions reversed to get $A_2B$ compound, e.g. K$_2$O, Rb$_2$S, Na$_2$Se, Li$_2$Te
The corundum or $D_{5h}$ crystal structure (sapphire $Al_2O_3$) has HCP ($ABAB\ldots$) planes of $O^2-$ anions. There are 30 ions per unit cell and the $Al_2O_3$ formula requires that these 30 ions be divided into 12 $Al^{3+}$ and 18 $O^2-$ ions. Thus there are how many formula units per cell?

According to $\rho$, $Al^{3+}$ has CN=6 (sits in octahedral site) which means $O^2-$ must have CN=4 ($T_d$).

Based on previous Table, stoichiometry will not allow the cation to sit in tetrahedral site (CN=4).

Also, two-thirds of the octahedral positions will be filled with $Al^{3+}$ ions, since the ratio of $Al^{3+}$ to $O^2-$ ions is 2:3 and there is one octahedral site per $O^2-$ anion.

Two close-packed $O^2-$ planes and the octahedral positions between these planes that will be filled with $Al^{3+}$ ions (top view sketched below):

Other examples: $Cr_2O_3$, $Ti_2O_3$, $\alpha-Fe_2O_3$, $Ga_2O_3$
Bond Hybridization – significant covalent bonding

– The hybrid orbitals can have impact if significant covalent bond character present
– For example in SiC
  • $X_{Si} = 1.8$ and $X_{C} = 2.5$

\[
\% \text{ ionic character} = 100\{1 - \exp[-0.25(X_{Si} - X_{C})^2]\} = 11.5\%
\]

• ~89% covalent bonding
• Both Si and C prefer $sp^3$ hybridization
• Therefore in SiC we get tetrahedral sites, Si has CN=4.
Zincblende (sphalerite) or B3 crystal structure (O sits on FCC sites)

\[ \frac{r_{Zn^{2+}}}{r_{O^{2-}}} = \frac{0.06}{0.138} = 0.435 \Rightarrow Octahedron? \]

- Size arguments predict Zn\(^{2+}\) in octahedron sites,
- In observed structure Zn\(^{2+}\) in tetrahedron sites

**Why is Zn\(^{2+}\) in tetrahedron sites?**
- Bonding hybridization of zinc favors tetrahedron sites

- So each Zn\(^{2+}\) has 4 neighboring O\(^{2-}\) (CN=4) and thus each O\(^{2-}\) must also have 4 neighboring Zn\(^{2+}\)

Since the ratio of Zn\(^{2+}\) to O\(^{2-}\) is 1:1 and there are two tetrahedral sites per O\(^{2-}\) ion, only one-half of the tetrahedral (T\(^{-}\) shown or T\(^{+}\)) positions will be occupied.

Exs: BN, GaAs, ZnO*, ZnS, SiC  *Note ZnO typically crystallizes in wurtzite or B4 crystal structure (O sits on HCP sites); we’ll return to this structure later when we discuss basis vectors.