6

Binary Compounds

CHAPTER PREVIEW

In this and the following chapter, we will describe the most important simple (binary) crystal structures found in ceramic materials. You need to know the structures we have chosen because many other important materials have the same structures and because much of our discussion of point defects, interfaces, and processing will use these materials as illustrations. Some, namely FeS_2, TiO_2, CuO, and Cu_2O, are themselves less important materials and you would not be the only ceramist not to know their structure. We include these oxides in this discussion because each one illustrates a special feature that we find in oxides. These structures are just the tip of the topic known as crystal chemistry (or solid-state chemistry); the mineralogist would have to learn these, those in Chapter 7, and many more by heart. In most examples we will mention some applications of the chosen material.

In traditional ceramic oxides, the anion is usually the larger ion, so we often think of a ceramic crystal structure as a three-dimensional (3D) array of anions with cations inserted in the interstices. Whether or not a particular structure is stable depends on Pauling's rules. We first review some of the important lattices, paying particular attention to the polyhedra that are formed by groups of anions. As the variety of ceramics being used in today's high-technology environment increases, some of the above assumptions cease to be valid. In certain oxides, the cation is larger than the anion and covalently bonded oxides and nonoxides cannot be treated as arrays of hard spheres. So we learn the rules and try to understand the exceptions. The concept of crystals being arrays of polyhedra will still work whether the bonding is ionic or covalent and whether the anion or the cation is larger.

In this and the following chapter, the *xyz*-axes in the schematics of cubic crystal structures lie along the cube edges; the length of the cube edge is the lattice parameter.

6.1 BACKGROUND

Using Pauling's rules, we can think of all crystal structures in terms of filling polyhedra. The polyhedra are those we discussed in Chapter 5. Particularly simple cases are the simple-cubic (sc), the hexagonal close-packed (hcp), and the face-centered cubic (fcc) lattices. In oxides like Al_2O_3 and MgO, the anion is the larger ion, which we consider to form a scaffold so that the cations fill the interstices between the anions. This thinking has a historical bias to it. It comes from the days when ceramics were light-element oxides. Such compounds automatically have smallish cations.

With the growing importance of ternary and tertiary oxides and the nonoxide ceramics, we have to be careful when making such assumptions. You must also remember that Pauling's rules apply to compounds in which the bonding is primarily ionic. In some compounds, the structure is the one predicted by Pauling's rules, but the reason may not be the one we gave when deriving the rules! In other words, if the bonding has a large covalent component, beware. Similarly, if the cation is large (e.g., in UO_2), we should not (though we sometimes do) consider the structure as a close-packed stacking of anions even if they do appear to lie on an fcc lattice.

Although we will examine only a few materials here, each one has the same structure as other important materials; we will list a few of these isomorphous materials. The examples chosen are also important because other crystal structures can be related to them with only a small distortion added to change the symmetry.

The logic of this chapter is summarized as follows:

CsCl	sc lattice with a two-atom basis
NaCl, GaAs	fcc lattice with a two-atom basis
CaF_2, FeS_2	fcc lattice with a three-atom basis
AlN	Hexagonal "close-packed" structure with a two-atom basis
Cu_2O	More complex but still cubic
TiO_2, CuO	Much more complex
Al_2O_3, CdI_2	"hcp" anions but not hcp structures
MoS_2	Layered material

6.2 CsCl

We start with the CsCl structure because it is the simplest possible, not because of its importance. The Bravais lattice of the CsCl structure is sc. We can view this structure in two ways:

- Two interpenetrating sc lattices, one of Cs^+ and one of Cl^-. The two sublattices are displaced by $\frac{1}{2}$<111>
- One sc lattice with a two-atom basis (Cs^+ at 0,0,0 and Cl^- at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$)

The concept of a sublattice is helpful when visualizing structures, but the phrase is sometimes used when the atoms do not really lie on a lattice. In this example, the lattice could be based on the positions of either the Cs^+ ions or the Cl^- ions.

We can check this structure against Pauling's rules. The ratio of the ionic radii (in pm) is

$$r_{Cs^+}/r_{Cl^-} = 170/181 = 0.94$$

As the ratio is >0.732 the Cs^+ should be 8-fold coordinated. It is clear from Figure 6.1 that the coordination number is indeed 8. This structure does not appear to occur for oxides since the (divalent) cation radius would need to be >102.5 pm (O^{2-} is 140 pm). It is not directional bonding that causes the structure to be adopted, just the packing requirements. This structure is the model B2 structure found in some important intermetallics like NiAl. It is also adopted by a number of halides having useful optical properties: as shown in Figure 6.2, CsBr, CsI, TlCl, and TlBr transmit in part of the ultraviolet (UV), all of the visible (the shaded region), and the near infrared (IR).

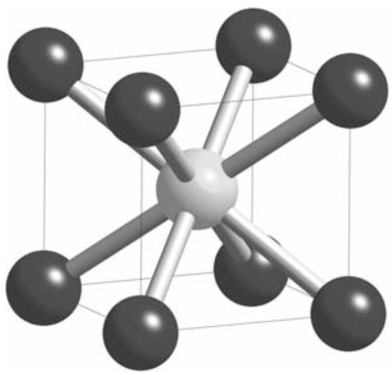

FIGURE 6.1 CsCl crystal structure. The polyhedron is the cube.

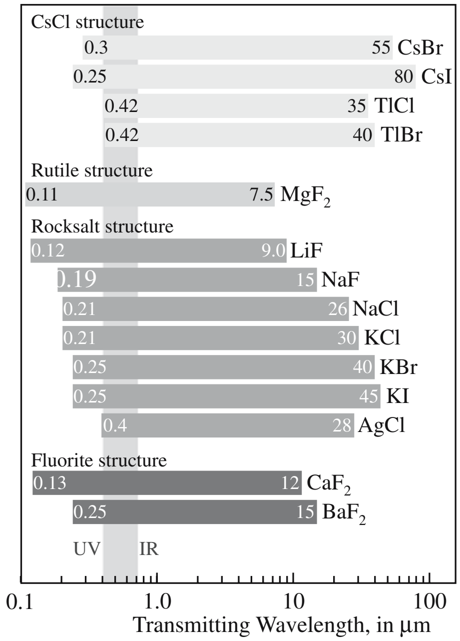

FIGURE 6.2 Range of transmittance for halide samples grouped by structure. (Each sample is 2 mm thick; 10% cut off.) The vertical band shows the visible range.

6.3 NaCl (MgO, TiC, PbS)

The NaCl (rocksalt or halite) structure is quite simple and is found for sulfides and carbides and some oxides, including MgO, CaO, SrO, BaO, CdO, FeO, and NiO. The anions are in an fcc arrangement and all the octahedral interstices are occupied by cations, as shown by Figure 6.3. The CN is 6 for both anions and cations.

The NaCl structure can be represented as follows:

- Two interpenetrating fcc lattices: one of anions and the other of cations displaced by $\frac{1}{2}$<001> or by $\frac{1}{2}$<111>
- An fcc lattice with a two-atom (Na-Cl) basis (Na^+ at 0,0,0 and Cl^- at $\frac{1}{2}$,0,0 or alternatively Na^+ at 0,0,0 and Cl^- at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$)

Of course, this structure is actually not close packed even though we have an fcc arrangement of anions. In the fcc metals each atom has 12 nearest neighbors (CN is 12); in NaCl each ion has six nearest neighbors (CN is 6), so the packing of the anions must be less dense than fcc. (By Pauling's rules, the octahedral interstice between the Cl^- ions must be larger than the minimum or the structure will be unstable.)

For MgO (magnesia or periclase), $r_{Mg^{2+}}/r_{O^{2-}} = 0.6$ so that the Mg must be surrounded by oxygen ions in an octahedral configuration. The bond strength (valence/coordination), $S_{Mg} = +\frac{2}{6} = +\frac{1}{3}$ so each O^{2-} must also be surrounded by 6 Mg ions. There is not a lot of choice on how to join them. Notice that $r_{Na^+}/r_{Cl^-} = 0.56$, which is also >0.414 but less than 0.732.

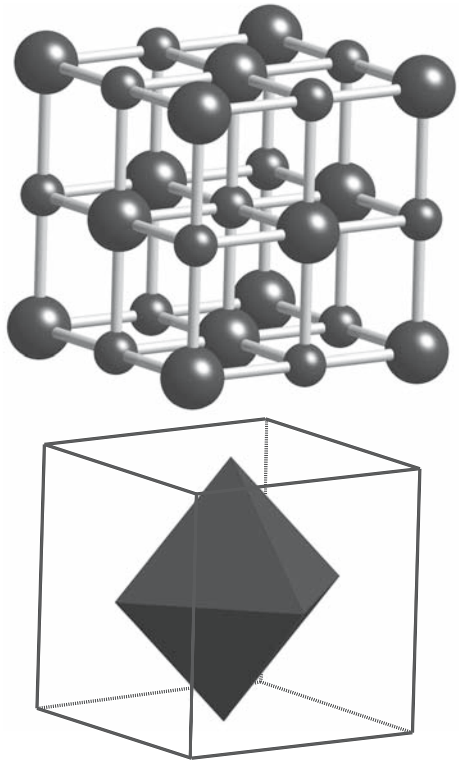

FIGURE 6.3 The NaCl crystal structure with Cl at 000. (Top) Ion positions; (bottom) an edge-sharing Cl octahedron.

FeO, CoO, MnO, and NiO are similar. NiO has the NaCl structure above its Néel temperature (523 K). Below this temperature magnetic ordering makes it rhombohedral. MnO and FeO behave similarly, but CoO undergoes a tetragonal distortion when the spins align; the Neél temperatures are 122, 198, and 293 K, respectively. Stoichiometric NiO is pale green. When heated in air it oxidizes and becomes a semiconductor.

Many of the oxides, carbides, and nitrides with the NaCl structure tend to be nonstoichiometric. Titanium monoxide exists over the range $Ti_{0.85}O$ to TiO, while FeO never occurs; it is always nonstoichiometric with a composition ranging from $Fe_{0.90}O$ to $Fe_{0.96}O$. As a consequence of these vacancies, the transition metal exists in two valence states, causing the oxide to exhibit semiconductor properties (as for NiO).

In the transition metal carbides and nitrides, think of the metal as being in the close-packed arrangement with the carbon or nitrogen atoms located in interstices. The coordination number can again be determined by the radius ratio, which in this case is given by r_x/r_m where r_x is the radius of the interstitial atom and r_m is the radius of the metal atom. Some values of atomic radius and radius ratios for transition metal carbides and nitrides are given in Table 6.1. The radius-ratio values given in Table 6.1 are consistent with a CN of 6 based on the critical radius ratios given earlier in Table 5.4. The interstitial atoms are located either in an octahedral site or in the center of a trigonal prism. For the transition metals, the tetrahedral interstices in the close-packed structures are too small for C or N.

TABLE 6.1 Atomic Radius and Radius Ratios for Some Carbides and Nitrides

Metal (M)	*Ti*	*Zr*
Atomic radius (nm)	0.147	0.160
C/M ratio	0.525	0.482
N/M ratio	0.511	0.470

All the octahedral interstitial sites are occupied in the NaCl structure. In general, when the radius ratio is less than 0.59 the metal atoms form very simple structures. The interstitial atom and its nearest metal neighbors comprise a structural unit. We can consider the structure of these materials as a metal structure with occupied interstitial sites. In the carbides and nitrides there are no C–C or N–N interactions.

Some of the nitrides and carbides such as NbC, TaC, and ZrN, which adopt the NaCl structure, are low-temperature superconductors. Although there is no evidence that this property is a direct consequence of the crystal structure, the crystal structure may play an important role.

Carbides with the NaCl structure have high hardness, are chemically inert, and have high melting temperature. The best-known example is TiC. It melts at 3147°C, has a Knoop hardness of 2470 kg/mm^2, a Young's modulus of 310 GPa, and is resistant to oxidation up to 1200°C (for more discussion of this see Chapters 16–18).

6.4 GaAs (β-SiC)

We can represent this structure as follows:

- Two interpenetrating fcc lattices one of anions and the other of cations displaced by $\frac{1}{4}$<111>
- An fcc lattice with a two-atom basis (one atom at 0,0,0 and the other at $\frac{1}{4},\frac{1}{4},\frac{1}{4}$)

This structure is rather open: the atomic packing factor (APF) for GaAs is only 0.41. In the GaAs structure each atom has only four nearest neighbors; the coordination number (CN) for both Ga and As is 4. The structure is shown in Figure 6.4 in 3D. The (110) projection is important because it clearly shows the tunnels along the <110> direction

II–VI, III–V, AND IV–IV

The classical name for this structure is zinc blende or sphalerite (ZnS).

GaAs, InP, InSb, etc. are not minerals.

Cubic SiC is known as carborundum or moissanite.

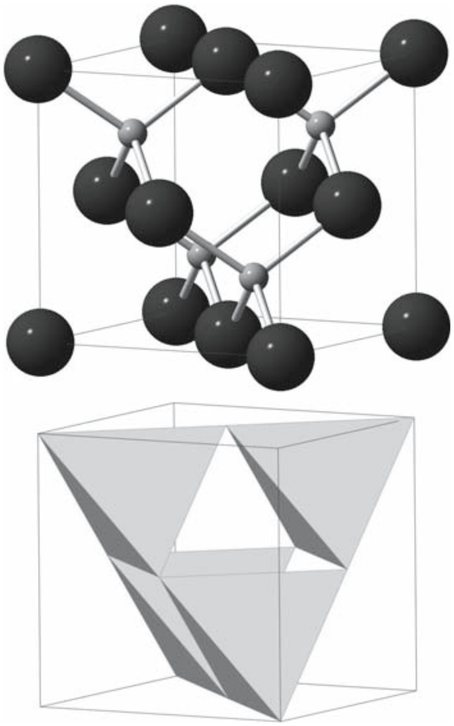

FIGURE 6.4 The zinc-blende crystal structure. (Top) Ion positions; (bottom) corner-sharing tetrahedra.

(remember that there are six equivalent <110> directions). You will see many high-resolution transmission electron microscope (TEM) images recorded with this sample orientation since it optimizes the detail seen in the image. An example is shown in Figure 6.5.

We can form the structure by stacking the anions in an fcc sequence and then filling half the tetrahedral interstices with cations. We could have chosen to stack the cations and then fill the interstices with anions, but the anions are usually larger. Other isomorphous materials include InP, InSb, GaP (known collectively as the III–Vs), and cubic SiC.

APPLY PAULING'S RULES

BeO $r_{\mathrm{Be}^{2+}}/r_{\mathrm{O}^{2-}} = 0.25$

ZnS $r_{\mathrm{Zn}^{2+}}/r_{\mathrm{S}^{2-}} = 0.34$

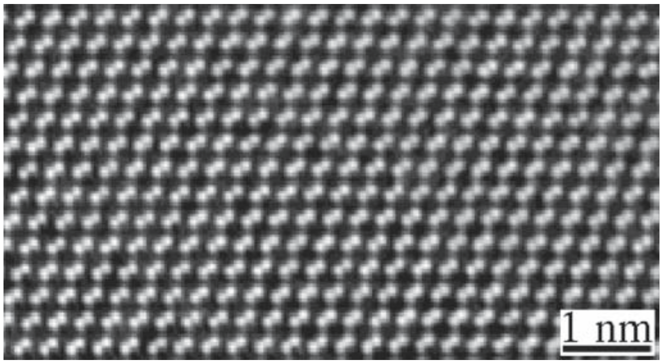

FIGURE 6.5 HRTEM image of GaAs showing the Ga-As 0.14-nm dumbbell.

TABLE 6.2 Relationship between Band Gap Energies and Bonding in III–V Semiconductors

Compound	E_g *(eV)*	*Ionic character in bond (%)*
AlP	3.0	9
GaP	2.35	6
AlAs	2.1	6
AlSb	1.55	4
GaAs	1.35	4
InP	1.30	4
GaSb	0.70	2
InAs	0.33	2
InSb	0.17	1

(% ionic character was calculated using Eq. 4.24)

Materials with a GaAs structure are usually semiconductors; this property is a direct consequence of the covalent bonding. In the III–Vs the band gap increases as the ionic component to the bonding increases, as shown in Table 6.2. If we replace all the Ga and all the As by C, Si, or Ge, we have the diamond-cubic (dc) structure of diamond, Si and Ge. Now the bonding is entirely covalent (and Pauling's rules would not work). We consider the GaAs structure again in comparison to AlN.

6.5 AlN (BeO, ZnO)

A second polymorph of ZnS is wurtzite (with a "t" in English but würzite in German). Many AB compounds such as AlN, GaN, BeO, and ZnO form in the wurtzite and zinc-blende structures under different conditions. We can form the wurtzite structure by arranging the anions with hcp stacking and then filling half the tetrahedral interstices with cations. The structure is illustrated in Figure 6.6. The CN for both anions and cations is 4. The first nearest-neighbor environment in AlN is identical to that in GaAs but in GaAs there are four identical <111> directions whereas AlN only has one [0001] direction. Consider BeO: the bond strength is $S_{\mathrm{Be}^{2+}} = +\frac{2}{4} = +\frac{1}{2}$. Each O^{2-} must be surround by four Be^{2+}. So the structure has to be created by stacking tetrahedra.

- For wurtzite we stack the tetrahedra ABABAB
- For zinc blende we stack the tetrahedra ABCABC

Although the theory clearly works beautifully, the catch is that the bonding between the Be^{2+} ions and the O^{2-} ions, or the Zn^{2+} ions and the S^{2-} ions, actually has a large covalent component; sulfides in particular do tend to be covalently bonded. So it is not really correct to apply Pauling's rules that were developed for ionic materials!

PACKING IN ZnS

We have hcp packing of S^{2-} ions for wurtzite and fcc packing of S^{2-} for zinc blende. In both structures Zn^{2+} ions are located in half the tetrahedral interstices to maximize their separation.

Another material that can be grown in either the wurtzite or zinc blende forms is SiC. The bonding here is mainly covalent (~88%) since both Si and C are group IV elements. SiC is special in that it is very difficult to produce in a single structure. It always has the chemical composition SiC, but tends to be a mixture of the two stacking sequences. The two structures are two of the polytypes of SiC. The cubic form of SiC is being produced as a diamond simulant known as moissanite.

FLUORITE-STRUCTURE OXIDES

c-ZrO_2, CeO_2, UO_2

BeO and AlN have both been used for electronic packaging because of their high thermal conductivity. BeO has the higher thermal conductivity, but its powder is highly toxic.

ZnO is a semiconductor where the conductivity depends on an excess of zinc atoms; its use in varistors relies on the properties of its grain boundaries as will be seen in Chapter 14. GaN is of great interest for manufacturing blue-green laser diodes and blue and green LEDs. In the future it will be ubiquitous in solid-state white lighting for energy-efficient domestic use and is already the best material available for green traffic lights.

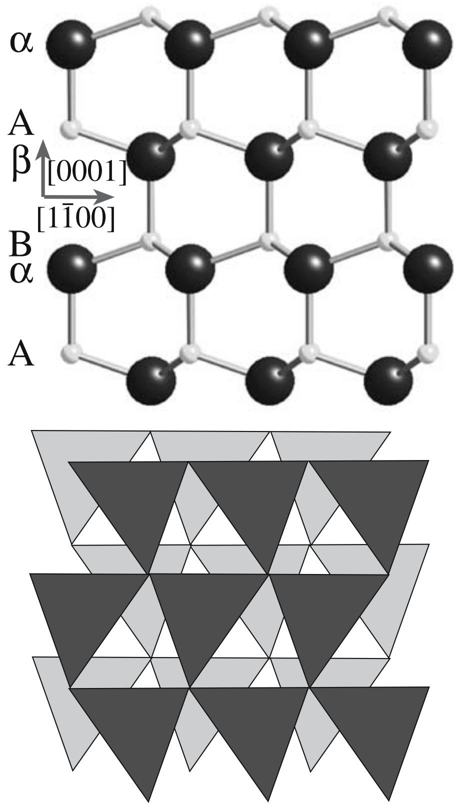

FIGURE 6.6 The wurtzite crystal structure viewed along [1120]. (Top) Ion positions showing the AαBβ stacking; (bottom) two interpenetrating arrays of corner-sharing tetrahedra. (Only one set is needed to construct the crystal.)

6.6 CaF_2

The mineral CaF_2 is known as fluorite, fluorspar, and Blue John. The ionic radii are $r_{Ca^{2+}} = 100$ pm and $r_{F^-} = 130$ pm, so $r_{Ca^{2+}}/r_{F^-}$ is ~0.8. By Pauling's rules; the Ca^{2+} ions should have CN = 8 and the F^- ions should have CN = 4. Since the fluoride ions are larger, we should think of the structure as a simple cubic stacking of the F^- ions with the Ca^{2+} ions filling every other cube interstice. However, you may remember the structure better by arranging the Ca^{2+} ions on an fcc lattice and then placing the F^- anions on the $\frac{1}{4},\frac{1}{4},\frac{1}{4}$ sites. These are the sites occupied by the Ga in GaAs, but now we occupy all such sites not just half of them. There is a large unoccupied cube interstice in the middle of the cell at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ (the unoccupied site in the other description). The fluorite structure is shown in Figure 6.7.

Cubic zirconia (CZ) is stable only at high temperatures or when stabilized by the addition of a dopant. CZ is a well-known diamond simulant in jewelry. Ceria and urania are both stable in the fluorite structure. In UO_2, our alternate description of the structure is now clearly the better one: the U^{4+} ion is large. The unoccupied cube interstice

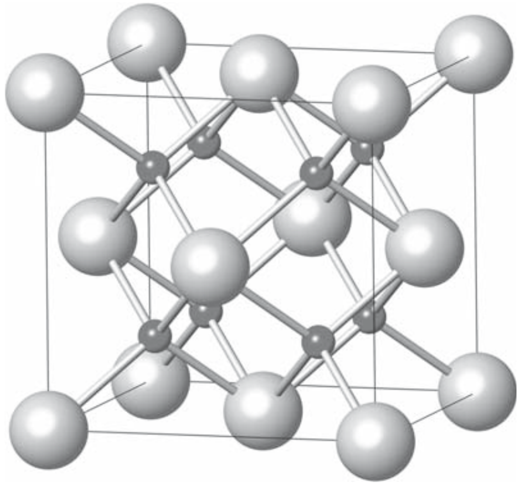

FIGURE 6.7 The fluorite crystal structure. The fluorine ions occupy the eight tetrahedral sites (or the Ca ions occupy half the cube sites with an empty one at the center of the unit cell).

at $\frac{1}{2},\frac{1}{2},\frac{1}{2}$ (in the center of the cell) in UO_2 is very important; it can accommodate nuclear fission products (like He) without straining the lattice. The oxides Li_2O, Na_2O, and K_2O are said to have an antifluorite structure because the location of the anions and cations is reversed relative to fluorite.

There is a great deal of interest in fluorides with the CaF_2 structure for optical applications. State-of-the-art production processes for semiconductor devices use deep-UV lasers to produce circuits with features as small as 130 nm. CaF_2 will then be the material of choice for semiconductor lithography. It is one of only a few materials that are transparent at the shorter wavelengths of deep-UV light (refer to Figure 6.2, CaF_2 is transparent down to 0.13 μm). The next major steps for lithography are expected to be systems using even shorter wavelength light, ultimately achieving feature sizes down to 70 nm when even CaF_2 will not suffice. You will also see top-of-the-line cameras using fluorite lenses so optical-quality CaF_2 will retain its value.

6.7 FeS_2

The structure of pyrite (fool's gold) is complicated but interesting. The Fe cations sit inside a sulfur octahedron. Three such octahedra then share a common vertex and there is no edge sharing. The S–S bond length within the octahedron is 0.307 nm or 0.332 nm, but the S–S bond that joins the octahedra together is only 0.218 nm long. The space group is $Pa\overline{3}$ with $a = 0.542$ nm. It is instructive to compare pyrite and NaCl. The pyrite structure is shown in Figure 6.8. Both appear to have an fcc cell with the Cl being replaced by an S_2 dumbbell, but the dumbbells point along different directions for each of the edges. The result is that NaCl belongs to the *m*3*m* class but pyrite belongs to the *m*3 class (still cubic but with a lower symmetry). Hence, NaCl has a 4-fold axis along [001] while FeS_2 does not, but you can find large (>4 cm on the side) single-crystal cubes of pyrite. Many binary metal chalcogenides (compounds containing S, Se, or Te) have an FeS_2 structure, as do a few oxides (CdO_2, α-K_2O, β-Na_2O). Note that S is below O in the periodic table—so we might ask what is the charge on Fe in FeS_2?

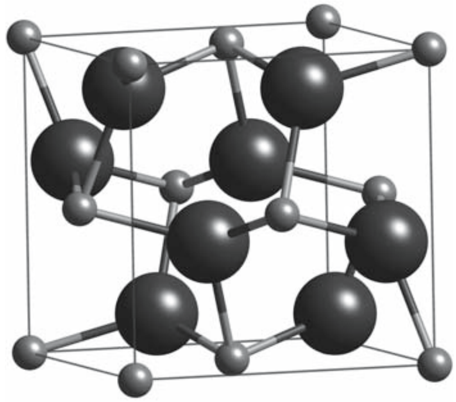

FIGURE 6.8 The FeS_2 crystal structure. The Fe ions occupy the fcc positions; the cubic cell also contains four S-S dumbells.

Some relationships between the NaCl structure and materials with related structures such as pyrite are shown in Figure 6.9. This schematic is one illustration of how a simple structure can be systematically distorted to produce a host of new crystal structures.

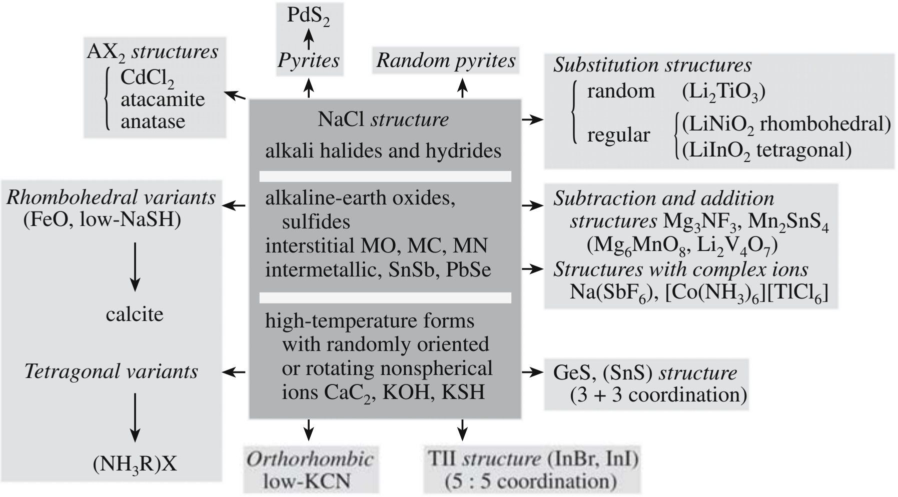

FIGURE 6.9 Schematic showing how two simple structures (NaCl and FeS_2) can be related to more complicated crystal structures.

6.8 Cu_2O

There are two main oxides of copper, Cu_2O and CuO. Cuprite, Cu_2O, is cubic with the *m*3*m* crystal group. It takes a little effort to imagine the structure. Start with the Si structure (dc) and replace all of the Si atoms with O^{2-} anions. Each anion is now surrounded by four other anions. Place a Cu^+ cation between every pair of anions. Then, where there is no tetrahedron in the dc structure, insert a new filled tetrahedron. We could alternatively have just created the tetrahedra of anions with cations between each one, and then stacked the maximum number (without changing their rotation) into the cube. This structure is difficult to visualize!

A simpler way of remembering the structure is shown in Figure 6.10. Four Cu ions form an fcc unit cell and the two O ions occupy two of the tetrahedral sites. The O^{2-} ions are much larger than the Cu^+ ions. (Remember how we think about the fluorite structure.)

This structure is particularly interesting because it consists of two linkages of tetrahedra that are rotated 90° to one another. The upper tetrahedron in Figure 6.10 is linked to another along the $[1\bar{1}0]$ direction at the top and along the [110] direction at the bottom (A connects to B). The second tetrahedron has the reverse arrangement.

Isomorphous oxides are Ag_2O and Pb_2O. Cu_2O and Ag_2O are p-type semiconductors because they contain excess oxygen atoms. The energy gap in Cu_2O is ~1.5 eV, and the impurity levels (acceptors) are about 0.3–0.6 eV above the valence band edge. Cuprite occurs naturally as a transparent red mineral.

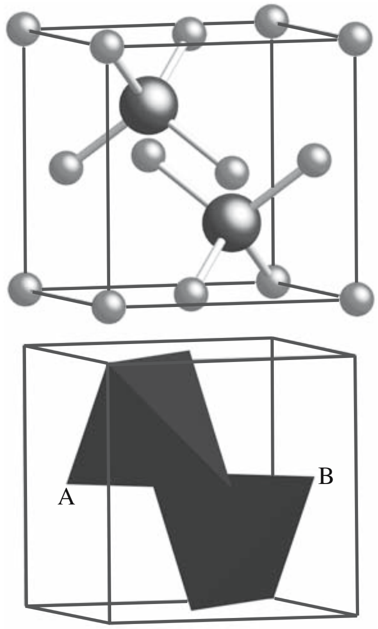

FIGURE 6.10 The Cu_2O crystal structure. (Top) Ion positions; (bottom) two "occupied" tetrahedra. The Cu ions sit at the fcc sites; two O ions "occupy" tetrahedral sites.

6.9 CuO

You might think CuO would have a simple structure (following CoO, NiO, and ZnO). Actually, tenorite (also known as melaconite) is monoclinic with the 2/*m* crystal class. The Cu atoms lie approximately in the middle of a square plane of four anions. Each anion is surrounded by four cations in what resembles a distorted tetrahedron. The square-plane coordination is the special feature of the cupric, Cu^{2+}, ion. Knowing the complex structure of these oxides can help in understanding the oxidation mechanisms of Cu. The square-plane coordination seen in this binary oxide will be relevant when we later think about complex copper-based oxides, such as YBCO.

6.10 TiO_2

TiO_2 exists as rutile, anatase, and brookite. These structures are different and we cannot think in terms of simply packing oxygen anions and filling the interstices. Each of the TiO_2 structures consists of Ti^{4+} cations in the center of oxygen octahedra. In rutile, which has tetragonal symmetry, the structure is constructed by linking octahedra. An octahedron is placed at each of the eight corners such that two are actually sharing an apex (e.g., at T). The six points on these octahedra are then connected by one rotated octahedron sitting in the center of the unit cell. The edges of the octahedra thus link together to give chains along the *z*-axis, as shown in Figure 6.11. Each Ti^{4+} is thus surrounded by six O^{2-} ions and each O^{2-} anion is surrounded by three Ti^{4+} ions. The structure is primitive tetragonal with $a = 0.459$ nm, $c = 0.296$ nm, and two formula units per unit cell. The easiest projection is (001) where we are looking along the 4-fold axis.

In anatase, the arrangement of the anions and cations is similar and the crystal is again tetragonal, but now each octahedron is somewhat distorted and shares four of its edges with other octahedra. In brookite, the structure is even more complicated with octahedra sharing both edges and corners. So the trend rutile–anatase–brookite is to ever decreasing symmetry.

Rutile is the simplest compound of a family of titanates that has high dielectric constants ranging from $\kappa \sim 100$ for rutile to several thousand for $BaTiO_3$. Of the other oxides that share the rutile structure, CrO_2 is ferromagnetic with a Curie temperature of 389 K, and VO_2 and MnO_2 are antiferromagnetic with Néel temperatures of 343 K and 84 K, respectively. SnO_2 (cassiterite) and several binary fluorides such as MgF_2 are isomorphous. A lesser known isomorphous compound is stishovite, which is a high-pressure form of SiO_2.

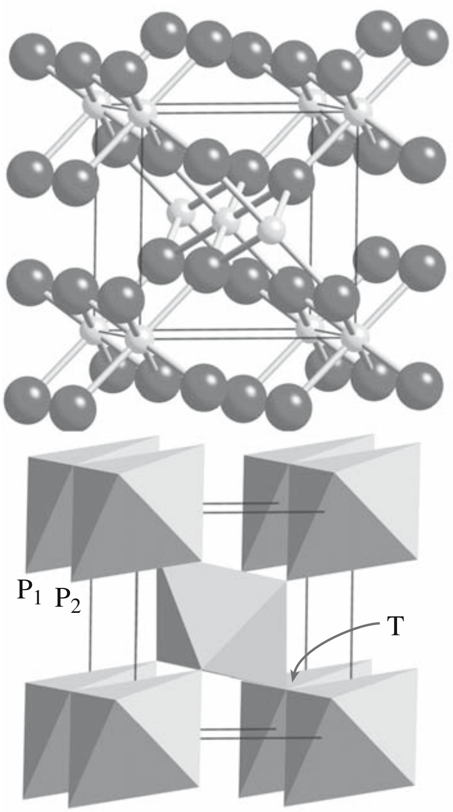

FIGURE 6.11 Rutile crystal structure viewed nearly parallel to the *z*-axis. Each of the pairs of overlapping octahedra (e.g., P_1/P_2) shares an edge. The two octahedra in the lower right thus have point T in common. The central octahedron touches each of the eight at the corners.

6.11 Al_2O_3

Alumina (the ceramic) or corundum (the mineral) refers to α-Al_2O_3. When it is doped with Cr^{3+} the mineral is called ruby; when doped with Ti ions we call it sapphire. Natural sapphire actually contains a combination of Ti^{4+} and Fe^{2+}, which compensate the charge difference. Some of the Fe^{2+} can be replaced by Ti^{2+} so that the Fe : Ti ratio can vary. (We may also have Ti^{3+} present.) Hematite, Fe_2O_3, is isomorphous with alumina; it actually has almost exactly the same c/a ratio. Ilmenite is closely related, but with Fe + Ti instead of Al + Al. Cr_2O_3 and Ga_2O_3 have a related structure. (In_2O_3 is completely different!)

The crystal structure of Al_2O_3 is trigonal with a $\bar{3}m$ crystal class, and has a pseudohexagonal oxygen sublattice (which is why we usually use a hexagonal cell and four-index Miller–Bravais notation) but the symmetry really is 3-fold, not 6-fold. In Al_2O_3 the oxygen ions have what can be thought of as hcp stacking with the Al^{3+} ions occupying two-thirds of the octahedral interstices (balancing the charge). The corundum structure is shown from two directions in Figure 6.12. Six parallel (0001) planes of oxygen ions are required to build the Al_2O_3 rhombohedral cell because the stacking is AαBβAγBαAβBγ; the Al^{3+} ions always sit in the C positions (thinking of the ABC fcc stacking), which is why we see the Al^{3+} ions when looking down the *c*-axis.

It is instructive to consider this structure in some detail. We can build it by stacking occupied octahedra (shown on the right). Each octahedron shares a face with the one above and the one below, but these are not regular octahedra. Pauling's rules say that it is not favorable to share faces of polyhedra. To compensate, the Al^{3+} cations move away from each other and toward the unoccupied octahedron (e.g., P_1 and P_2) as can be seen in Figure 6.12; the oxygen anions move close together (e.g., the boxed group labeled S) to shield the nearby positive charges. The result is that the (0001) "plane" of Al^{3+} cations actually lies on two distinct (0001) planes. This also means that there are two different oxygen–oxygen ion distances in the octahedra. We saw a similar effect in Section 6.7.

Specific letters are used to designate several of the common crystallographic planes in corundum (Table 6.3). These different orientations are shown schematically in Figure 6.13. It is useful to know this convention, especially

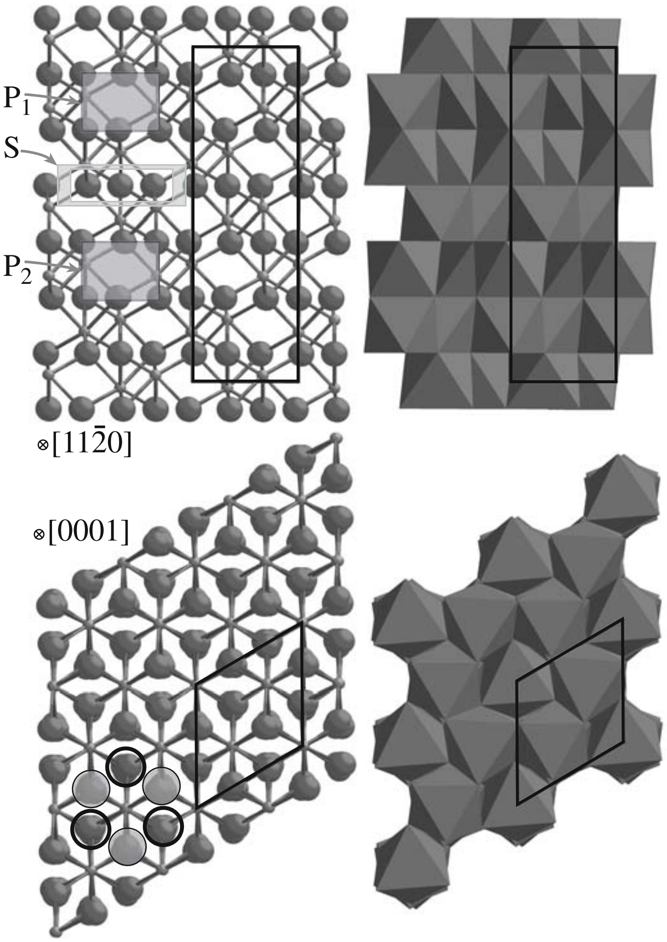

FIGURE 6.12 The sapphire crystal structure. (Top) [11$\bar{2}$0] view; (bottom) [0001] view; (left) atomic models; (right) stacking octahedra. P_1 and P_2 are two unoccupied octahedra. S is a triangle of more closely spaced O^{2-} ions. Open circles in the lower left show the AB stacking of the anions. The unit cell is outlined for both projections.

TABLE 6.3 Common Crystallographic Planes in Sapphire

Plane "name"	*Miller–Bravais index*	d *spacing (nm)*
a	$(11\bar{2}0)$	0.2379
c or basal plane	(0001)	0.2165
m	$(10\bar{1}0)$	0.1375
n	$(11\bar{2}3)$	0.1147
r	$(1\bar{1}02)$	0.1740

if you want to order or use single-crystal sapphire substrates.

Aluminum oxide is by far the most widely used compound with this structure. As a single crystal it is used in watch bearings and pressure-resistant windows. Hot-pressed powders are employed as electrical insulators, windows or radomes transparent to microwaves, envelopes for lamps, and electrical devices. In polycrystalline form it is also the basis of refractory bricks, crucibles, and spark-plug insulators.

6.12 MoS_2 AND CdI_2

MoS_2 and CdI_2 are based on the hcp structure. In molybdenite, the Mo atoms are located in the positions corresponding to the unit cell of the hcp structure. An S–S pair is centered along the *c*-direction directly opposite the Mo atoms, giving the structure shown in Figure 6.14. The stacking sequence can be written as AbA BaB, where the capital letters denote the S atoms and the lowercase letters the Mo atoms. The coordination number of the metal atom is 6, as it is in the TiO_2 and CdI_2 structures. Thus, we would expect that phases with r_M/r_X between 0.41 and 0.73 would form any of these structures. However, the more ionic compounds form the rutile structure, while the more covalent compounds have the CdI_2 structure. Those in which the bonding is intermediate adopt the MoS_2 structure.

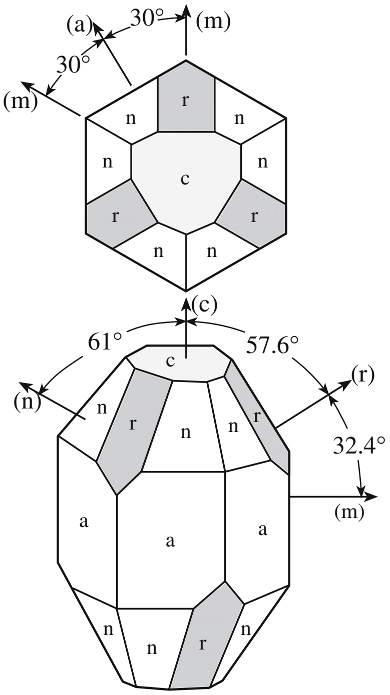

FIGURE 6.13 The location of important planes in sapphire.

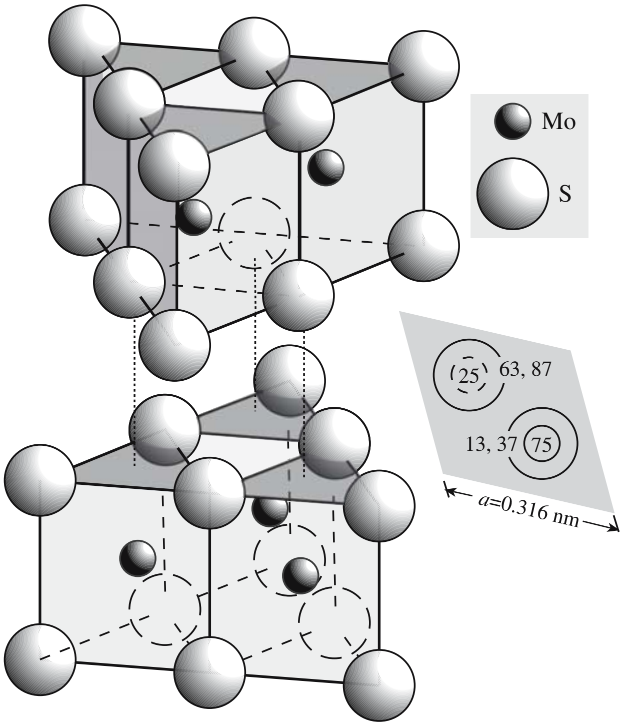

FIGURE 6.14 The crystal structure of molybdenite. The S ions stack AABB while the Mo ions occupy half the trigonal prisms in each S "sandwich".

Several of the Mo and W chalcogenides adopt the molybdenite structure, but MoS_2 is the most interesting phase and is an excellent (dry) lubricant. It is instructive to compare the MoS_2 structure to the structure of graphite, which is shown for comparison in Figure 6.15. The unit

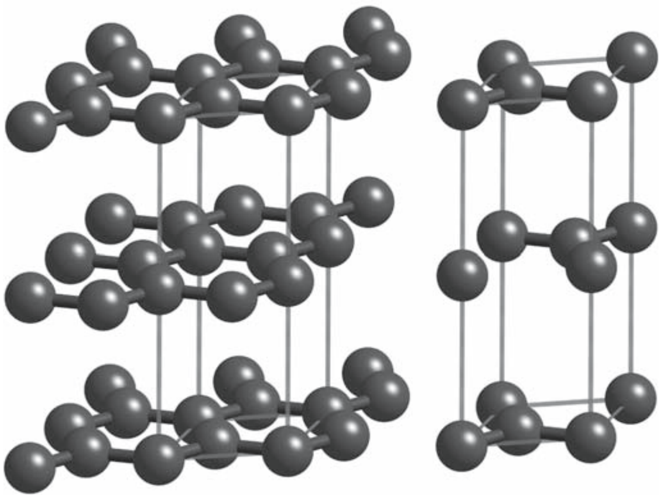

FIGURE 6.15 The crystal structure of graphite. The C atoms form hexagonal rings as seen on the left. A unit cell is outlined and is shown alone on the right.

cell of graphite is clearly hexagonal and has lattice parameters $a = 0.2456$ nm and $c = 0.6696$ nm. The C–C bond length is 0.142 nm in the sheets and 0.335 nm between sheets. The six-membered rings are stacked to give an ABAB stacking sequence. It is the long bond distance in the *c*-direction that gives graphite similar properties as a solid lubricant. (Actually, it is the weak bonds between pairs of basal planes that cause the bonds to be long, which is the underlying reason.) As expected, graphite has highly anisotropic properties. The properties of graphite within the sheets are similar to those of a metal, whereas the properties perpendicular to the sheets are more like those of semiconductors.

Since in MoS_2 and graphite the interlayer, van der Waals, bonding is very weak, the structures can also exist in a rhombohedral form with a stacking sequence AbA BaB CcC; other layer materials naturally adopt this structure.

The crystal structure of BN is closely related to that of graphite except that the atoms in one layer lie directly above those in the next and the six-membered rings are made up of alternating B and N atoms.

This structure can also be derived from the hcp structure by replacing the metal atoms in the unit cell by I atoms and by adding Cd atoms at the corners of the unit cell. Thus, the I^- ions sit in an hcp arrangement with the Cd^{2+} ions between them. The more covalent AB_2 phases tend to form the CdI_2 structure. Thus, the larger polarizable iodides and bromides form this structure with highly polarizing cations, while the fluorides favor the rutile structure.

6.13 POLYMORPHS, POLYTYPES, AND POLYTYPOIDS

Polymorphs are materials that have the same chemical composition but different crystal structures. Many ceramic materials show this behavior, including SiO_2, BN, $BaTiO_3$, ZrO_2, and BeO. Transitions between the different polymorphs may occur as a result of changes in temperature or pressure. The relationships between the polymorphic forms of silica are shown in Figure 6.16 with the corresponding transformation temperatures. These are not the only known phases of SiO_2. At pressures around 2 GPa, quartz transforms into coesite. At even higher pressures, around 7.5 GPa, coesite transforms to stishovite. The high-pressure forms have been prepared experimentally and are also found at the famous Cañon Diablo Meteor site in Arizona. (We will examine these structures further in Chapter 7.)

When an element exists in different solid phases we refer to the phases as allotropes. Graphite and diamond are two allotropes of carbon.

Polytypism is a special—one-dimensional—type of polymorphism in which the different crystal structures assumed by a compound differ only in the order in which a two-dimensional layer is stacked. The effect is common in layer structures (e.g., MoS_2, graphite, and layer silicates). Silicon carbide (SiC), a ceramic material of considerable importance, displays the richest collection of polytypic forms. More than 200 SiC polytypes have been determined. Figure 6.17 shows the structural relationship between five of the different polytypes. Table 6.4 gives the stacking sequence and lattice parameters for the polytypes.

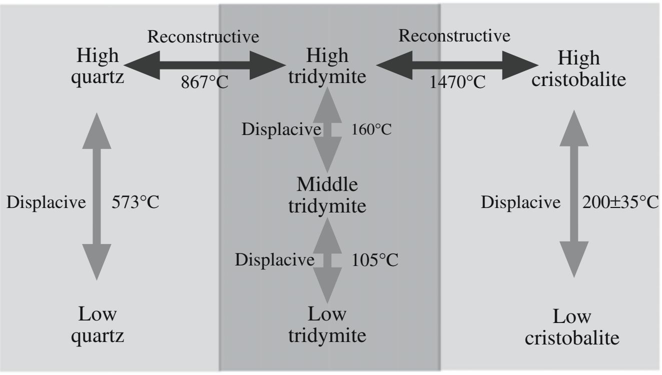

FIGURE 6.16 Schematic of how the polymeric forms of silica can be converted into one another by displacive or reconstructive structural transformations.

You will notice in Figure 6.17 that we have translated the usual cubic representation of the zinc blende cell into a rhombohedral one, which can be compared directly with the unit cells of the other SiC polytypes. A way of viewing the cubic (3C) cell as a rhombohedral cell is shown in Figure 6.18. The former cubic-cell diagonal has now become the *c*-axis of the corresponding rhombohedral cell. Of course, the arrangement of the atoms remains unchanged.

You will also notice that we introduced a new notation scheme in Table 6.4. The Ramsdell notation is frequently used when referring to different polytypic forms and describes the stacking sequence in these complex structures. The notation consists of a number and a letter. The number indicates the number of layers in the sequence. The letter indicates the structure type (C = cubic, H = hexagonal, R = rhombohedral). At one extreme we have the zinc blende SiC (3C) with pure cubic stacking in the [111] direction. At the other extreme we have wurtzite SiC (2H) with pure hexagonal stacking in the [0001] direction. The other polytypes have either H or R stacking sequences. For example, the carborundum III (B5) structure in Figure 6.17 has the Ramsdell symbol 4H—the sequence consists of four layers, then repeats, and the structure is hexagonal.

This chapter discusses the structure of a series of binary compounds that are also used as models for other compounds. All ceramics students must learn some of these structures by heart, but it is equally important to

TABLE 6.4 Relationship between Polytypes in Silicon Carbide

Structure	Strukturbericht	Stacking sequence	Lattice parameters a (nm)	c (nm)	Ramsdell notation
Wurtzite	B4	AB	0.3076	0.5048	2H
Zinc blende	B3	ABC	0.308	0.755	3C
Carborundum III	B5	ABAC	0.3076	1.004	4H
Carborundum II	B6	ABCACB	0.3080	1.509	6H
Carborundum I	B7	ABACBCACBABCBAC	0.3080	3.781	15R

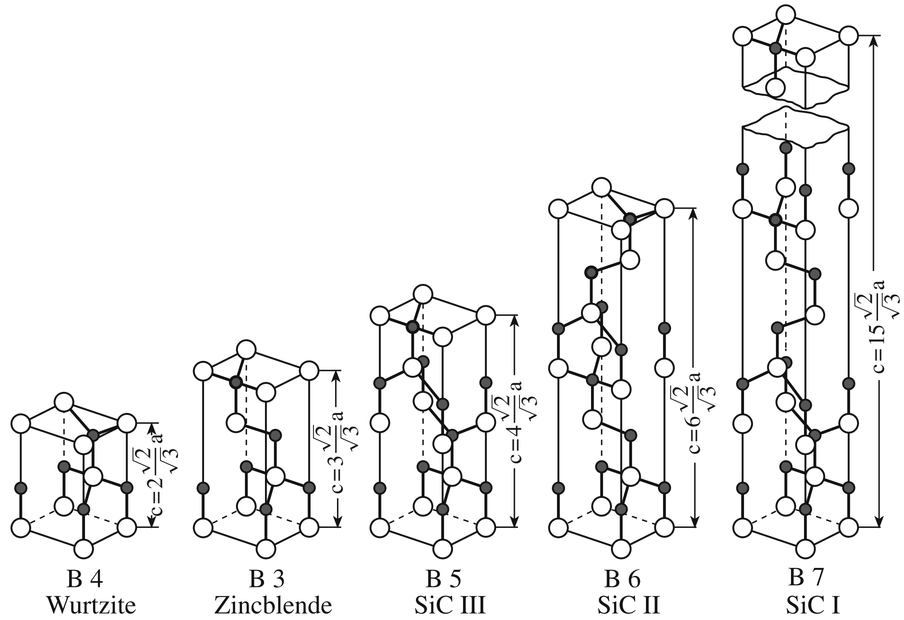

FIGURE 6.17 The stacking sequence for five SiC polytypes.

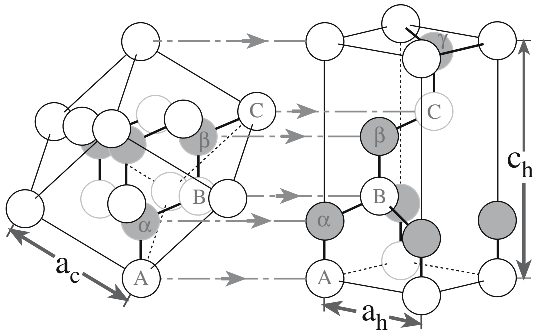

FIGURE 6.18 Relating the cubic and rhombohedral unit cells for zinc blende.

know the reason we chose these structures and how they relate to Pauling's rule (Chapter 5). Also remember that Pauling's rules were developed for ionic materials, so any covalent component may compromise the predictions. The polyhedra found in these simple structures reappear in much more complex structures as will be seen in Chapter 7. Each of the compounds has an application as illustrated here, but we concentrate more on those in later chapters. As an example, CaF_2 used to be known as an interesting structure and a semiprecious stone. That it would today be grown as 200-mm-diameter crystals for 135-μm UV lithography would not have been imagined a few years ago. Although it is used for its optical properties, the orientation of the crystal must be controlled because the optical properties depend on the crystal orientation. The best large sapphire windows (with minimum birefringence) are cut from (0001) crystals. The crystal structure of crystalline materials controls most of the properties of these materials.

CHAPTER SUMMARY

To really understand ceramic materials, you must know their basic crystal structures. Then you can picture the polyhedra such as the tetrahedron and the octahedron and know what we mean when we talk about linking them, distorting them, substituting them, etc. Always keep in mind Pauling's rules. We have discussed the most important of the structures of the binary compounds: you must know CsCl, NaCl, GaAs, AlN, CaF_2, MoS_2, and Al_2O_3 by heart. We have also included FeS_2, Cu_2O, CuO, CdI_2, and TiO_2 in part because these materials are becoming more important in their own right, but also because they provide insight into many related binary compounds. Throughout this chapter and in Chapter 7 we have drawn many of the diagrams using CrystalMaker. This is an affordable program for the Mac and PC and should be available to every student taking any ceramics or mineralogy course. It is today's equivalent of the real (wooden) ball-and-(steel) stick models that used to be passed around the class but rarely were taken home to your dorm-room. It allows you to switch from ball-and-stick to polyhedra at the click of a mouse.

PEOPLE IN HISTORY

Bragg, W.H. and son W.L. Bragg did not discover X-ray diffraction, but they realized that it could be used to determine the structure of crystals. The first structure they solved was that of NaCl. They won the 1915 Nobel Prize in Physics "for their services in the analysis of crystal structure by means of X-rays." Aside from the Braggs, the other father and son tandem of Nobel laureates is the Thomsons (Sir Joseph Thomson, Physics 1906, and his son George Paget Thomson, Physics 1937) and the Siegbahns (Karl Manne Siegbahn, Physics 1924, and his son Kai Siegbahn, Physics 1981).

Coes, Loring, a high-pressure scientist, gave his name to the high-pressure form of quartz. He first synthesized coesite in 1953 in the Norton Laboratories.

Moissan, Ferdinand Frédéric-Henri began researching diamond synthesis in 1889. His idea was to produce diamonds by passing an electrical current through a sample of iron and sugar charcoal, then rapidly quenching it in cold water. However, after one experiment Moissan did isolate very small diamond octahedral crystals. After his death in 1907 it was revealed that one of Moissan's assistants had planted natural diamonds to make Moissan feel better. Moissan did actually make SiC, which was later given the name moissanite.

IUCr is the International Union of Crystallography. The Society publishes the journal *Acta Crystallographica*. IUCr recorded: "the very first specialized X-ray diffraction meeting with international representation was an informal one and was held at Ewald's mother's house on the Ammersee, Germany, in 1925. In addition to Ewald, the small group included W. L. Bragg, L. Brillouin, C. G. Darwin, P. J. W. Debye, R. W. James, M. von Laue, I. Waller and R. W. G. Wyckoff."

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Bragg, W.L. and Claringbull, G.F. (1965) *Crystal Structure of Minerals*, Cornell University Press, Ithaca, Volume IV of the series The Crystalline State. If you have time to look at the original work, see this in your library.

CrystalMaker. www.crystalmaker.co.uk We repeat this information: you should try it.

Deer, W.A., Howie, R.A., and Zussman, J. (1996) *An Introduction to the Rock-Forming Minerals*. 2nd edition, Prentice-Hall, Englewood Cliffs, NJ. This is a classic for good reason.

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Hyde, B.G. and Anderson, S. (1989) *Inorganic Crystal Structures*, Wiley, New York. The structures of many crystals are beautifully described and related in this book.

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Xu, X., Beckman, S.P., Specht, P., Weber, E.R., Chrzan, D.C., Erni, R.P., Arslan, I., Browning, N., Bleloch, A., and Kisielowski, C. (2005) "Distortion and segregation in a dislocation core region at atomic resolution," *Phys. Rev. Lett.* **95**, 145501.

EXERCISES

6.1 Draw and label (the ions and at least three directions) the [100], [111], and [110] projections for rocksalt, GaAs, CsCl, and fluorite.

6.2 Draw and label (the ions and at least three directions) the [0001], [1$\bar{1}$00], and [11$\bar{2}$0] projections for hematite.

6.3 Draw and label (the ions and at least three directions) the [0001], [1$\bar{1}$00], and [11$\bar{2}$0] projections for ZnO.

6.4 Estimate the radius of the cubic interstice in UO_2. Discuss this result using Pauling's rules.

6.5 You know the crystal class of FeS_2 and its space group. Explain the relationship.

6.6 Prove that the APF for GaAs is 0.41. The atomic radii for Ga and As are 0.135 and 0.125 nm, respectively. The lattice parameter is 0.565 nm.

6.7 The coordination number for silver and copper ions in Ag_2O and Cu_2O is four. This is quite unusual for these ions. What would you expect the coordination number to be based on the sizes of the ions and how might you explain the observed differences, if any. The ionic radii of the ions are given in Table 4.6.

6.8 Does rutile obey Pauling's rules?

6.9 How do the densities of high cristobalite and silica glass compare? You will need to dig for the data on this one—the library or the Internet.

6.10 NaCl, TiC, and PbS all have the same structure. Are they all good examples of Pauling's rules in action?