# 7

# Complex Crystal and Glass Structures

## CHAPTER PREVIEW

This chapter is separated from the previous one just to make it less overwhelming! We've demonstrated the principles in Chapter 5 and considered some of the simpler ceramic structures in Chapter 6. Now we are considering structures that have more than two chemically different atoms in the unit cell (such as $YBa_2Cu_3O_7$) although some still have only two components. We include materials (such as $SiO_2$) where covalent bonds are particularly important and encounter materials involving secondary bonds such as van der Waals interactions (especially in the clay minerals).

It is a little difficult to learn these structures by heart, but some, such as cristobalite and perovskite, you should know. For others, you may survive by just knowing the basic ideas involved. This emphasizes the reason for this chapter (and Chapter 6)—if you understand the building blocks, you can better appreciate the properties of more complex structures that are composed of combinations of such building blocks. The logic behind the order in which these are discussed is first cubic, then the silicates (starting with silica), then the complicated ones, and finally some new materials that challenge our perception of what is a ceramic.

Glass has often been treated separately from ceramics, but today few programs in materials science have the time for a specialized course on glass. We include a discussion of glass structures in this chapter because they link so closely with the crystal structure of crystalline silicates and the general concept of coordination polyhedra. We discuss the properties of glass later. Remember that the structure of glass is *not* random; it just lacks long-range order. We have point defects and other defects in glass just as we do in crystals; the challenge is to define the nondefective structure that we can relate them to. What makes a point defect in glass a defect and not just part of the glass?

A common mantra throughout this chapter is "diagrams are essential." A difficulty is that you generally need more than one diagram (view) to appreciate a three-dimensional (3D) structure. Computer programs can make the 3D aspects much more apparent.

In this and the previous 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.

## 7.1 INTRODUCTION

In most simple metal–oxide structures, $r_M << r_X$ and the structures can be built up by considering a nearly close-packed arrangement of oxygen ions with cations located in interstices. The ionic radius ratios given earlier are useful and provide a means of predicting the coordination number (CN) of a particular compound, and often the predictions are in good agreement with observed values. In cases where the observed CN differs greatly from the expected value, such as 12 for $K^+$ in mica, $KAl_3Si_3O_{10}(OH)_2$, it is probable that the other ions present play the most important part in determining the arrangement.

The ions that are close to the transition values of the radius ratio can show variations in CN. An example is the $Al^{3+}$ ion ($r_{Al}/r_O = 0.38$), which sits inside oxygen tetrahedra in many aluminosilicates but inside octahedra in others (as is the case for $Al_2O_3$). The $Al^{3+}$ ion has CNs of both 4 and 6 in sillimanite, both 5 and 6 in andalusite, but only 6 in kyanite even though all three are stable minerals, and all have the composition $Al_2SiO_5$. Another example is the $Zr^{4+}$ ion ($r_{Zr}/r_O = 0.51$), which is octahedrally coordinated in several crystals, e.g., $CaZrO_3$ (isomorphous with perovskite), but has a CN of 8 in zircon, $ZrSiO_4$. As Pauling said, the size of the ion depends on the site that it occupies.

Table 7.1 lists some deviations from the CN predicted by radius ratios. Where the observed CN is larger than predicted, there is a gain in electrostatic energy by increasing the number of nearest neighbors. This gain is larger

C.B. Carter and M.G. Norton, *Ceramic Materials: Science and Engineering*,
DOI 10.1007/978-1-4614-3523-5_7, © Springer Science+Business Media New York 2013

**TABLE 7.1 CN and Bond Strength, S, of Various Cations with Oxygen**

| *Ion* | $r_M$ (pm) | $CN_{theory}$ | $CN_{obs}$ | *S* |
|---|---|---|---|---|
| $B^{3+}$ | 16 | 3 | 3, 4 | 1 or 3/4 |
| $Li^+$ | 53 | 6 | 4 | 1/4 |
| $Si^{4+}$ | 29 | 4 | 4, 6 | 1 |
| $Al^{3+}$ | 38 | 4 | 4, 5, 6 | 3/4 or 1/2 |
| $Ge^{4+}$ | 39 | 4 | 4, 6 | 1 or 2/3 |
| $Na^+$ | 73 | 6 | 4, 6, 8 | 1/6 |
| $Zr^{4+}$ | 51 | 6 | 6, 8 | 2/3 or 1/2 |
| $Ca^{2+}$ | 71 | 6, 8 | 6, 7, 8, 9 | 1/4 |
| $Ce^{4+}$ | 57 | 6 | 8 | 1/2 |
| $K^+$ | 99 | 8, 12 | 6, 7, 8, 9, 10, 12 | 1/9 |

than the energy expended in deforming the surrounding ions. Remember that the ions are not rigid spheres. Where the observed CN is smaller than predicted, there is often an appreciable amount of covalent character to the bonding. Covalent bonds are strongly directional.

Why so much about silicates? We spend effort on silicates not just because they are the main constituents of the earth's upper mantle (and therefore the geological materials we most readily see) but because they are really ubiquitous (even when you don't at first realize it) and therefore provide many of our raw materials. We suspect that silicates also have an enormous range of unexplored applications. Silicates also link in with the second unusual topic for such a chapter, namely glass: many glasses are silicates that lack long-range order.

## 7.2 SPINEL

The mineral spinel is $MgAl_2O_4$. Spinels have the general formula $AB_2O_4$, although later we also write it as $AO.nB_2O_3$, where *n* describes the nonequimolarity. Bragg and Nishikawa actually solved the spinel structure independently in 1915. The spinel structure is so important because the magnetic ferrites are spinels. For the ferrites, we express the chemical formula as $MO.Fe_2O_3$, where M is a divalent metal ion, such as Mn, Ni, Fe, or Co (or a mixture of such ions).

Although structurally quite simple, spinel has a large number of atoms or ions associated with each lattice point in its Bravais lattice. The Bravais lattice is fcc, and the unit cell contains a total of 56 ions (32 oxygen ions). There are four lattice points per fcc unit cell and thus 14 ions associated (two formula units) with each lattice point.

**SOME IMPORTANT SPINELS**

| | |
|---|---|
| $\gamma$-$Fe_2O_3$ | Maghemite |
| $MgAl_2O_4$ | 'Real' spinel |
| $NiFe_2O_4$ | A classic ferrite |
| $Fe_3O_4$ | Magnetite |

In spinel we often think of the $O^{2-}$ ions as sitting on the fcc lattice sites. Actually, they are generally slightly displaced from these exact positions. Considering the cations and thinking of $MgAl_2O_4$, the $Al^{3+}$ ions now occupy some of the octahedral sites, with the $Mg^{2+}$ ions being located on tetrahedral sites. This arrangement is the "normal" as opposed to "inverse" spinel structure; most spinels are not exactly normal! Note that the arrangement of the oxygen ions is essentially the same as in MgO, but now some of the octahedral and some of the tetrahedral interstices are occupied instead of only the octahedral ones.

- *Normal spinel:* The $A^{2+}$ ions occupy only tetrahedral sites, and the $B^{3+}$ ions occupy only octahedral sites.
- *Inverse spinel:* All the $A^{2+}$ions and half the $B^{3+}$ ions sit on the octahedral sites; the tetrahedral sites are occupied now by the other half of the $B^{3+}$ ions.

The arrangement of the cations is such that the lattice parameter of the spinel $MgAl_2O_4$ is close to twice that of the corresponding MgO. If we think of the spinel cubic unit cell as divided into eight cubes, these smaller cubes would be almost exactly the size of the MgO unit cell. This means that six parallel {111} planes of oxygen ions are required to construct the rhombohedral cell, rather than three.

Looking at some ionic radii, we can understand why the same structure can be formed with Ni or Co substituting for Mg. Similarly, Fe or Cr can substitute for Al.

$$O^{2-}: 140\,\text{pm},\ Mg^{2+}: 72\,\text{pm},\ Ni^{2+}: 69\,\text{pm},\ Co^{2+}: 74\,\text{pm}$$

$$O^{2-}: 140\,\text{pm},\ Al^{3+}: 53\text{pm},\ Fe^{3+}: 65\text{pm},\ Cr^{3+}: \ 62\text{pm}$$

If we look at this structure along a [110] direction (Figure 7.1A, B), we can see the tetrahedra and octahedra. Remember that the anions are in an fcc stacking sequence, so this is a close-packed direction for the O ions. Spinel thus shows particularly clearly how a structure can be built up by systematically filling some of the octahedral (O) sites and some of the tetrahedral (T) sites. The apparently touching tetrahedra are actually at different heights in this projection, so they do not share an edge. The lines $P_1$ and $P_2$ remind you where the edge-on {111} planes lie. If we rotate the structure through 90° about the horizontal $[1\bar{1}0]$ axis, we reach the [001] projection shown in Figure 7.1C.

We can look at the structure in several ways. In Figure 7.1B, the cell has been divided into eight distinct layers of ions. This sequence is PqRsTuVw, where the upper case refers to mixed $O^{2-}$ plus

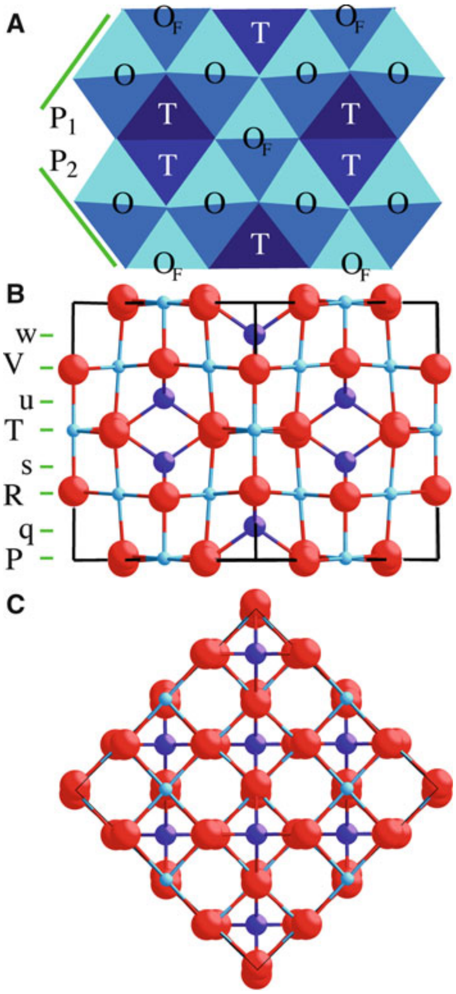


**FIGURE 7.1.** Spinel crystal structure. The 32 anions in the unit cell form eight slightly distorted fcc oxygen lattices. The cations are then distributed with one tetrahedron occupied in each "sub-cell" (rather like $Cu_2O$). The 16 octahedral sites are then distributed in rows along one <110> direction or the orthogonal one depending on the layer (V,R or T, P in "b").

octahedral cation layers, and the lower case refers to the tetrahedral cations. This method of building the structure emphasizes that there are only two different "planes" of ions to stack! The row of octahedral sites actually rotates 90° every 1/4 cell (i.e., every two layers). Hence, layers P and T are shifted relative to one another but are rotated 90° relative to R and V. The structure is effectively shifted by ¼ $[1\bar{1}0]$ every four layers (half way up the cell). (We return to this stacking in Chapter 14).

How did Bragg determine the spinel structure, and how can you distinguish normal and inverse? X-ray diffraction measures the distribution of electrons and hence allows us to deduce atom position by measuring the structure factor. The positions $x_n$, $y_n$, and $z_n$ are fractional coordinates of atoms in the unit cell. Because the structure factor, $F$, depends on $x_n$, $y_n$, and $z_n$, the value of $F_{\text{normal}} \neq F_{\text{inverse}}$.

In $\gamma$-$Fe_2O_3$, the other cation is a "vacancy"; maghemite is known as a defect spinel and is related to the other important defect spinel $\gamma$-$Al_2O_3$ (although there may be other complications involving $H^+$ ions in this case). The Fe ions in magnetite occupy both tetrahedral and octahedral sites so it is $FeFe_2O_4$ but we haven't specified which ion ($Fe^{2+}$ or $Fe^{3+}$) sits where. Spinels are notorious for being nonequimolar ($n \neq 1$, which does not mean the same as nonstoichiometric). When the formula is written as $AO.nB_2O_3$, the value of $n$ can vary from 1 to 3.5 depending on A, B, and T.

## 7.3 PEROVSKITE

With a general formula $ABO_3$, the A cation and the anions effectively form an fcc array with a large octahedron in the center of the cell but no available tetrahedra (because of the charge). The ideal perovskite structure is simple cubic, and this is what we generally imply when we refer to the perovskite structure. The mineral perovskite is $CaTiO_3$ and is actually orthorhombic at room temperature, only becoming cubic at temperatures above 900°C. Other ceramics with the perovskite structure include $BaTiO_3$, $SrTiO_3$, and $KNbO_3$, each being written in the general form $ABO_3$. Don't confuse the structure with that of ilmenite, $FeTiO_3$, which is related to the alumina structure.

The perovskite structure is shown in Figure 7.2A. Looking at the ionic radii, we can see a trend. The $O^{2-}$ anion and the larger cation ($A^{2+}$) have similar radii so that the structure is not just determined by $O^{2-}$. The larger cation and the anion combine to form a "close-packed" arrangement, with the smaller cation, $B^{4+}$, sitting in the oxygen octahedral interstices. The octahedra then link together by sharing corners, as shown in Figure 7.2B.

### $BaTiO_3$ AND $KNbO_3$

| A | B | O |
|---|---|---|
| $R_{Ba^{2+}} = 136$ pm | $R_{Ti^{4+}} = 61$ | $R_{O^{2-}} = 140$ pm |
| $R_{K^{+}} = 138$ pm | $R_{Nb^{5+}} = 64$ | $R_{O^{2-}} = 140$ pm |

### $CaCO_3$ AND $CaTiO_3$

The carbonate is an inorganic salt. The anion is $CO_3^{2-}$, which is quite like a sphere although it actually has 3-fold symmetry and is shown as a triangle in Figure 7.3. This anion and the $Ca^{2+}$ are arranged in similar way to NaCl but with a threefold distortion.

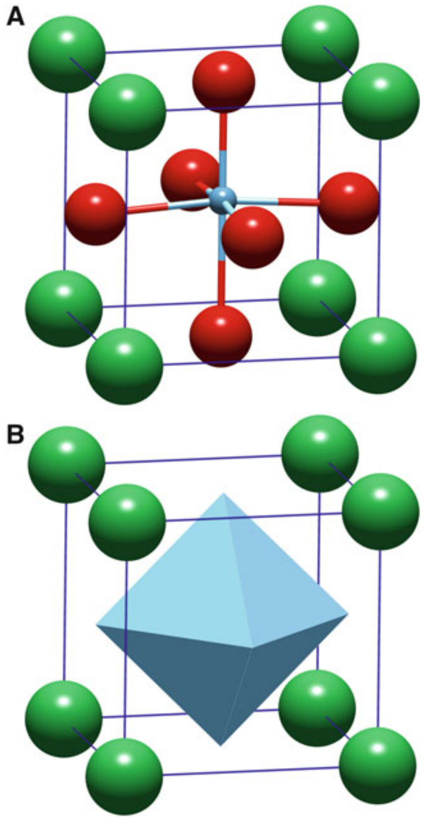


**FIGURE 7.2.** Perovskite crystal structure. The lattice is simple cubic, with several cations able to occupy the central octahedron. (A) Atomic model. (B) Polyhedron.

The bond strength is given as

$$\mathrm{Ti-O} = +4/6 = 2/3; \quad \mathrm{Ca-O} = +2/12 = 1/6$$

Each $O^{2-}$ anion coordinates with two $Ti^{4+}$ and four $Ca^{2+}$ cations so that the total bond strength is

$$2 \times 2/3 + 4 \times 1/6 = +2$$

Barium titanate ($BaTiO_3$) is the prototype ferroelectric material. It has the ideal perovskite structure above 120°C. At temperatures below 120°C, the small cation ($Ti^{4+}$) shifts off its ideal symmetrical position at the center of each octahedral interstice. This shift creates an electric dipole; it polarizes the structure electrically, which in turn causes the material to become noncubic; it changes the cell dimensions. Spontaneous electrical polarization in the absence of an applied electric field is termed *ferroelectricity*. The link between electric field and mechanical deformation of the unit cell is known as the *piezoelectric effect*: it allows us to convert an electrical signal to a mechanical one and vice versa. This shift actually has the same origin as the flexibility of this structure: many ions can fit in the central ocahedron.

The perovskite structure is particularly important for several reasons:

- Many perovskites are ferroelectric.
- Many perovskites are piezoelectric.
- Many perovskites have a high dielectric constant.

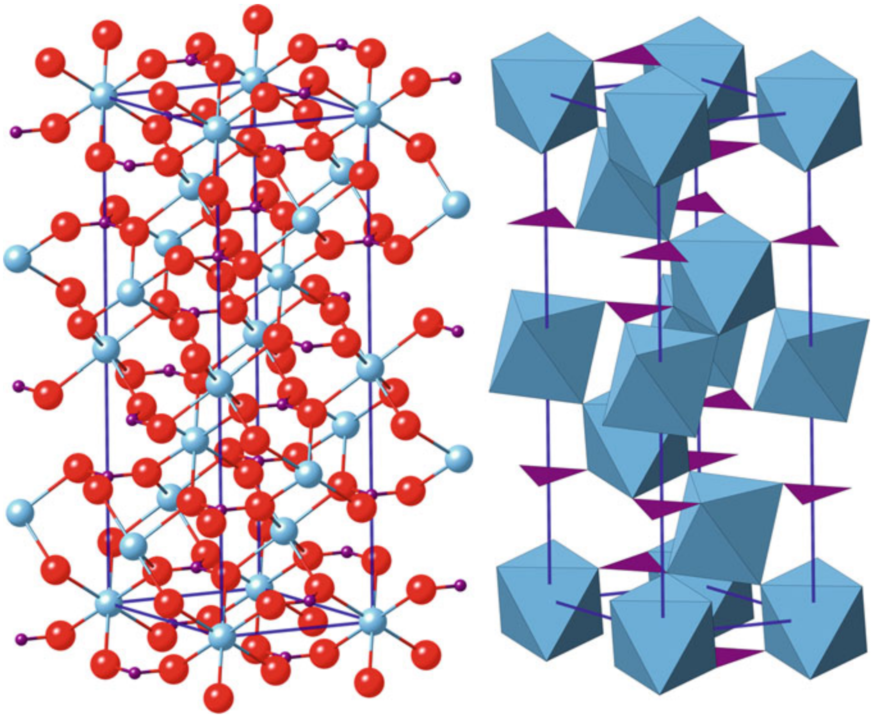


**FIGURE 7.3.** Crystal structure of calcite. The $Ca^{2+}$ cations sit in the octahedral site; the $CO^{2-}$ ions are represented as a triangle that each links six octahedra. The octahedra each has one of two orientations and “stacks” in an ApBqCr sequence giving the $\bar{3}$ symmetry and producing the c lattice parameter of 1.71 nm (a is 0.50 nm).

The perovskite structure is also of interest to mineralogists. A mineral with the perovskite structure of composition close to $MgSiO_3$ is believed to be the predominant mineral in the lower mantle (depths of about 600 km) of the Earth. The perovskite structure of $MgSiO_3$ is stable only at very high pressures.

Perovskites have also received much attention since 1986 because the superconducting oxide YBCO contains perovskite structural elements. The importance of this structure was again realized in 1993 when the phenomenon of colossal magnetoresistance (CMR) was discovered in a range of manganate ceramics with a layered perovskite structure similar to that found in YBCO and other high-temperature superconductors.

## 7.4 THE SILICATES AND STRUCTURES BASED ON $SiO_4$

We can start by considering ionic radii and Pauling's rules.

$$r_{Si^{4+}}/r_{O^{2-}} = 0.40/1.40 = 0.29 < 0.41$$

Thus, tetrahedral coordination is expected, and the bond strength, $S$, is +1 (= $+^4/_4$). The $(SiO_4)^{4-}$ units are the building blocks for all silicates; each $O^{2-}$ ion is coordinated with two $Si^{4+}$ions, so the tetrahedra join at corners. Actually, there is a very large covalent component too so that the Si–O bond is very strong (it is only ~40% ionic). Thus, Pauling's rules don't really apply, and we just talk about the $SiO_4$ unit and take account of the charge separately.

Some possible linkages of $SiO_4$ tetrahedra are illustrated in Figure 7.4. This is a key idea in understanding silicates. We can either keep the $SiO_4$ tetrahedra separate or link them to one another. If we link them, then we can form chains or rings. Then we can join rings to make sheets or join chains to make double chains. Units formed by these combinations are listed in Table 7.2.

To give you an idea of the variety of structures that are then possible, a discussion of just the structures (not properties—just structures) of rock-forming minerals consisting of isolated $SiO_4$ tetrahedra is the subject of a 900-page text. Table 7.3 lists some examples of the classes of silicates with special structures. Table 7.4 gives an idea of the complex crystallography involved. Clearly, we can't go through all the ideas of silicates as this is an enormous field.

**TABLE 7.2 Linking $SiO_4$ Tetrahedra to Make Silicates**

| # | *Structure unit* | *Structure formula* |
|---|---|---|
| 0 | $[SiO_4]^{4-}$ | Orthosilicates |
| 1 | $[Si_2O_7]_n^{6-}$ | Pyrosilicates |
| 2 | $[SiO_3]_n^{2n-}$ | Pyroxene chain |
| 2.5 | $[Si_4O_{11}]_n^{6n-}$ | Amphibole<br>Note difference between this and infinite-sheet clays ($Si_2O_5$) |
| 3 | $[Si_2O_5]_n^{2n-}$ | |
| 4 | $[SiO_2]_n^{0}$ | 3D network |

#Number of shared vertices

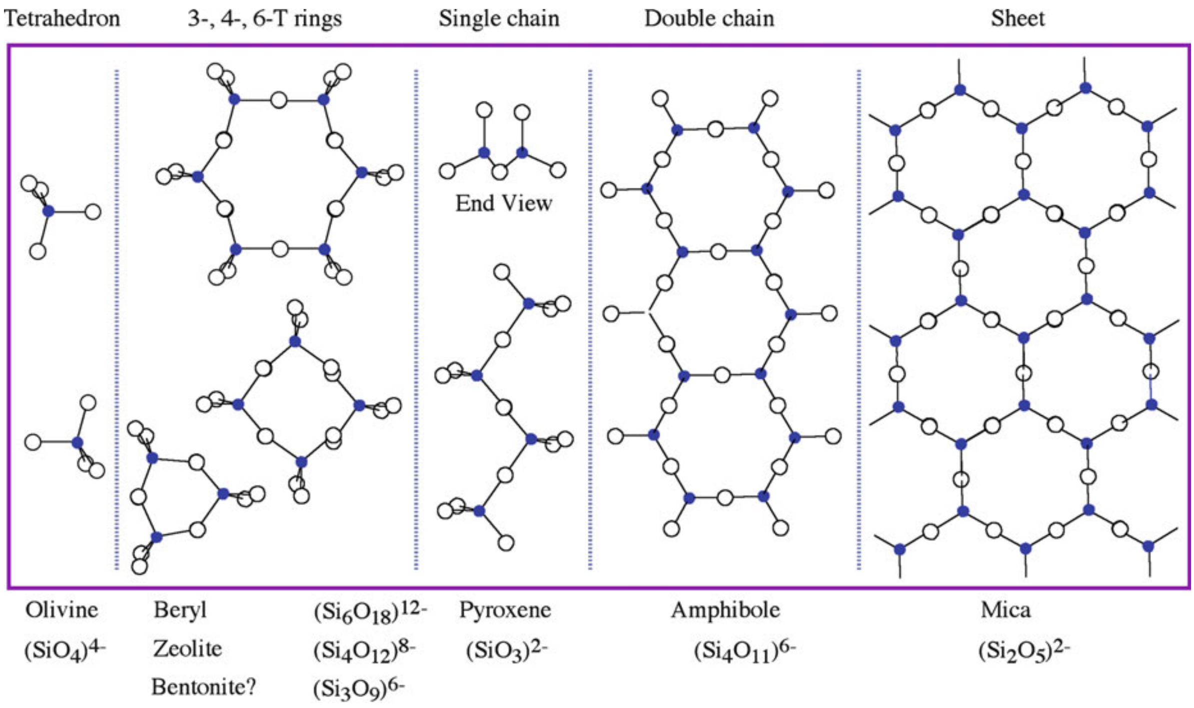


**FIGURE 7.4.** Arranging $SiO_4$ tetrahedra in different silicates. The exception is the sheet that extends indefinitely in all directions in the plane. These are the best known ways of combining (or not) the $SiO_4$ tetrahedra.

**TABLE 7.3 Examples of Silicate Structures**

| | | |
|---|---|---|
| Orthosilicates | Forsterite<br>Fayalite<br>Monticellite<br>Grossular | Olivine and garnet refer to groups containing many well-known minerals |
| Ring silicates | Beryl<br>Cordierite | Rings of $SiO_4$ tetrahedra connected at a corners |
| Chain silicates | Enstatite<br>Diopside | Pyroxenes are single chain compounds |
| Sheet silicates | Muscovite<br>Biotite<br>Talc | Mica and kaolinite refer to groups of sheet silicates |
| Framework silicates | Anorthite | Groups include the quartz minerals, feldspars and zeolites |

**TABLE 7.4 Some Silicates**

| | | | | |
|---|---|---|---|---|
| Olivine | $(Mg,Fe)_2SiO_4$ | P mmm | Orthorhombic | Island silicate |
| Zircon | Zr $SiO_4$ | I 4/mmm | Tetragonal | Island silicate |
| Beryl | | C 6/mmm | Hexagonal | Island silicate |
| Cordierite | | C mmm | Orthorhombic | Ring silicate |
| Tourmaline | | R 3 m | Trigonal | Ring silicate |
| Enstatite | | Pmmm | Orthorhombic | Chain silicate |
| Talc | | C 2/m | Monoclinic | Layer silicate |
| Mica | | C 2/m | Monoclinic | Layer silicate |
| Cristobalite | | F m3m | Cubic | Framework silicate |
| Albite | | $C\bar{1}$ | Triclinic | Framework silicate |
| Anorthite | | $P\bar{1}$ | Triclinic | Framework silicate |

You should know the general principles, the bonding, etc., and the language!

A special feature of the silicates is that it is often quite easy to replace the cations that are outside the $SiO_4$ tetrahedra. This leads to the idea of *isomorphous replacement*. We can even replace the $Si^{4+}$ in the $SiO_4$ tetrahedron with other similar-size ions (such as $Al^{3+}$) having the same oxygen coordination. The idea is that $r_{Al}{}^{3+}/r_{O}{}^{2-} = 0.36$, which is close to 0.41. $Al^{3+}$ can have 6 or 4 coordination. To balance the charge, we also need to replace some $Na^+$ (say) by $Ca^{2+}$. The following are two well-known examples:

- Forsterite and fayalite are structurally almost identical and thus form a continuous solid solution, with $Mg^{2+}$ gradually being replaced by $Fe^{2+}$ across the series (as we go to fayalite).
- The feldspar minerals fall into two main series: the alkali (K-Na) feldspars, where we gradually replace $Na^+$ by $K^+$ across the series, and the plagioclase (Ca-Na) feldspars, where there is a continuous variation in composition by substituting $Ca^{2+} + Al^{3+}$ for $Na^+ + Si^{4+}$.

**TABLE 7.5 Some Densities**

| *Oxide* | *a* (nm) | *c* (nm) | *Density in g/cm$^3$* |
|---|---|---|---|
| High quartz | 0.501 | 0.547 | 2.65 |
| High tridymite | 0.503 | 0.822 | 2.26 |
| High cristobalite | 0.713 | | 2.32 |
| MgO | | | 3.59 |
| $Al_2O_3$ | | | 3.96 |

## 7.5 SILICA

Silica has many different polymorphic forms (see Section 6.13). We discuss three forms of $SiO_2$, namely quartz, tridymite and cristobalite (note the spelling). For each form, at low temperatures (the α phase) we find a structure that is a distortion of the high-temperature form (the β phase). In each case, changing from the α to β structure involves a displacive phase transformation; the atoms need to move only slightly relative to one another. However, to change from one form to another requires breaking bonds. This process is much more difficult and is known as a reconstructive phase transformation.

The Si–O–Si arrangement of ions does not always lie exactly on a straight line, especially for the low-temperature forms. If the bonding were purely ionic, the line would be straight and the $O^{2-}$ should lie exactly in the middle: the reason in each case is that we want to maximize the electrostatic attractive forces and minimize the electrostatic repulsion. However, the Si–O bond is ~60% covalent, so there is a strong tendency toward directional bonding. The different forms of silica have different densities, each being much less dense than the more ionic oxides, as shown in Table 7.5.

The structure of high cristobalite, showing the highest symmetry, is illustrated in Figure 7.5 as arrangements of atoms and as a stacking of tetrahedra. The $Si^{4+}$ cations sit in the same positions as the Si atoms in the dc Si structure. An $O^{2-}$ anion is located between each and every pair of $Si^{4+}$ cations! In high tridymite, the $Si^{4+}$ cations sit on wurtzite sites instead of zinc blende, and the $O^{2-}$ anion again sits between the cations! You can appreciate the movement that is needed to transform tridymite to cristobalite. When tridymite is found, it always contains small amounts of impurities. It is possible that these impurities are necessary to stabilize the structure.

## 7.6 OLIVINE

The olivine minerals are orthosilicates: the $SiO_4$ tetrahedra are isolated from one another, meaning that the tetrahedra do not share oxygen ions. The structure is seen from two directions in Figure 7.6, which shows that the structure can be envisioned in a way that relates it to spinel and alumina. The hexagonal ABAB stacking of the anions seen in "A" is

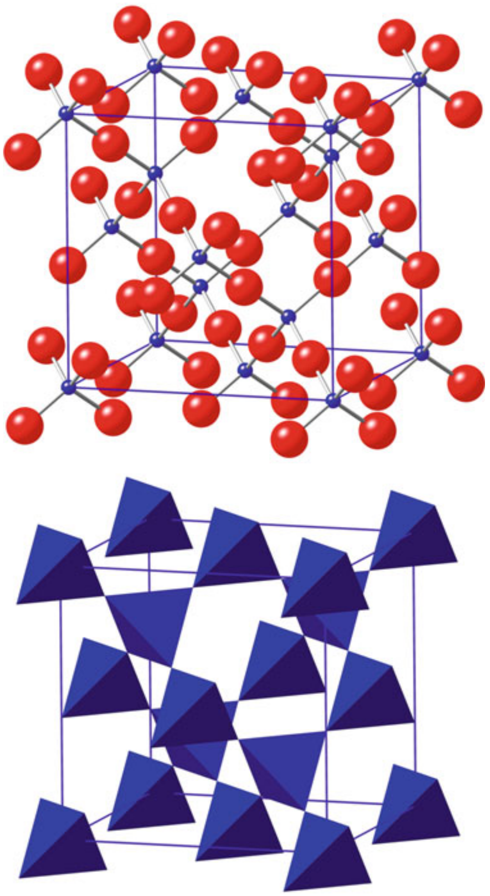


**FIGURE 7.5.** Crystal structure of cristobalite. The most symmetrical for $SiO_2$ having cubic symmetry (m3m) and a lattice parameter of 0.72 nm.

just like alumina, as is the view from normal to these close-packed layers shown in "B." Unlike alumina, some of the cations are in tetrahedral sites, and others are in octahedral sites, like spinel. But unlike spinel, the two types of site are present between every close-packed layer of anions. Like spinel, the pairs of tetrahedra are not actually sharing edges, as appears to be the case in "A." The result of this distribution of cations is that the crystal structure is orthorhombic, with the b lattice parameter by far the longest, at 1.02 nm; the a and c lattice parameters are 0.48 and 0.60 nm, respectively. The $O^{2-}$ anions at the corners of the tetrahedra are linked by O-A-O bonds (A being Mg or similar); some tetrahedra point up, others point down. In forsterite, this $Mg^{2+}$ ion is located at the center of an octahedron just as it is in MgO.

The best-known composition of olivine, the light green gemstone peridote, is $(Mg_{0.9}Fe_{0.1})_2SiO_4$. The olivines are a group of minerals showing isomorphous replacement.

- Forsterite, $Mg_2SiO_4$; with up to 10% Fe replacing Mg
- Fayalite, $Fe_2SiO_4$; with up to 10% Mg replacing Fe
- Monticellite, $Ca(Mg,Fe)SiO_4$; the Ca and Mg/Fe give an ordered stacking
- Tephroite, $Mn_2SiO_4$; a rare mineral that may contain Zn, Fe, or Mg substituting for Mn

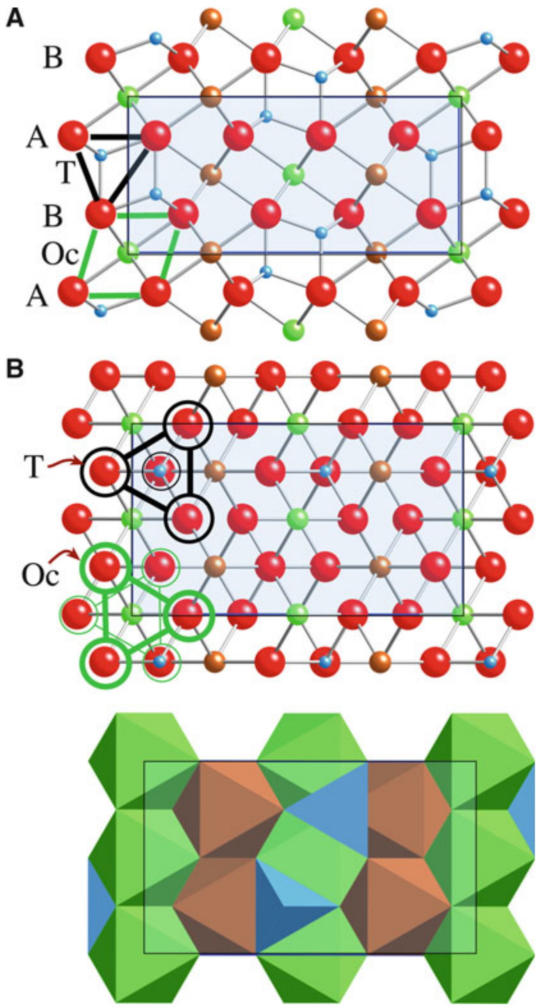


**FIGURE 7.6.** Crystal structure of olivine, an orthosilicate. (A) View along [001]. (B) View along [100]. Examples of octahedra and tetrahedra are outlined in both figures. Typified by forsterite, $Mg_2SiO_3$.

Olivine is one of the most important materials in the earth sciences. The structure has been rediscovered recently because of its importance for cathode materials in lithium-ion batteries (see Chapter 37).

## 7.7 GARNETS

Garnet refers to both the garnet group of silicates and the garnet structure, which is also adopted by nonsilicates. Some names and chemical compositions of garnets are summarized in Table 7.6. The garnets have the general formula $A_3B_2(DO_4)_3$, where A and B refer to divalent and trivalent cations; D is Si in the case of silicates. In the nonsilicates, the structure is interesting because the same trivalent ion can sit in two very different sites, the A site and the B site. Important nonsilicate garnets include YAG (a laser host material) and YIG (a magnetic garnet).

It may help to remember the composition of YAG, say, by remembering that it is $4(X_2O_3)$ where X is a combination of trivalent cations. The structure is formed

**TABLE 7.6 Examples of Garnets**

| *Garnet* | *Formula* | *Alternate* | *a* (nm) |
|---|---|---|---|
| Pyrope | $Mg_3Al_2Si_3O_{12}$ | $Mg_3Al_2(SiO_4)_3$ | 1.146 |
| Alamandine | $Fe(II)_3Al_2Si_3O_{12}$ | $Fe(II)_3Al_2(SiO_4)_3$ | 1.153 |
| Spessartine | $Mn_3Al_2Si_3O_{12}$ | $Mn_3Al_2(SiO_4)_3$ | 1.162 |
| Grossular | $Ca_3Al_2Si_3O_{12}$ | $Ca_3Al_2(SiO_4)_3$ | 1.185 |
| Andradite | $Ca_3(Fe(II),Ti)_2Si_3O_{12}$ | $Ca_3Fe(III)_2(SiO_4)_3$ | 1.205 |
| Uvarovite | $Ca_3Cr_2Si_3O_{12}$ | $Ca_3Cr_2(SiO_4)_3$ | 1.202 |
| Hydrogrossular | $Ca_3Al_2Si_2O_8$ $(SiO_4)_{1-m}(OH)_{4m}$ | | |
| YAG | $Al_3Al_2Y_3O_{12}$ | $Al_5Y_3O_{12}$ | |
| YIG (I: iron) | $Fe_3Fe_2Y_3O_{12}$ | $Fe_5Y_3O_{12}$ | |
| GGG | $Ga_3Ga_2Gd_3O_{12}$ | $Ga_5Gd_3O_{12}$ | |

by combining $DO_4$ tetrahedra and $BO_6$ octahedra (at the corners). The 3D framework thus formed contains cavities that can be viewed as distorted cubes of a triangular dodecahedron, as shown in Figure 7.7. The A cation sits in the large dodecahedral site (CN = 8). This is a very flexible crystal structure that has certainly not been fully exploited due to its complexity. However, many new garnets are now being produced, such as erbium-doped yttrium scandium gallium garnet [$(Y,Er)_3Sc_2Ga_3O_{12}$, or Er:YSGG] single crystals. These materials are being used for diode-pumped solid-state lasers that radiate in the 3-µm range.

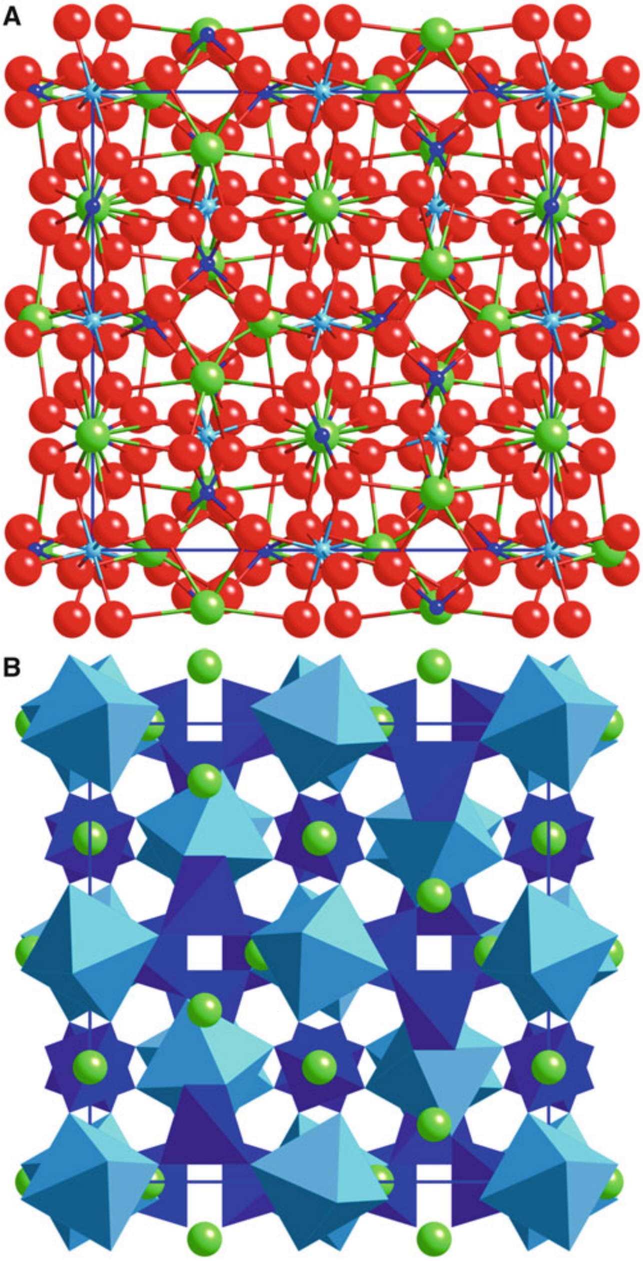


**FIGURE 7.7.** Crystal structure of garnet. The general formula is $A_3B_3(CO_4)_3$ where C is Si for the silicates. The B cation sits in an octahedral site, and the largest cation A is located in a dodecahedron. The bcc unit cell has a lattice parameter of ~1.1 nm. With 20 atoms in the chemical formula, there are 160 atoms in the unit cell.

## 7.8 RING SILICATES

The ring silicates are also known as the metasilicates. Well-known ring silicates are beryl, tourmaline, and cordierite. The first two are mainly thought of as gemstones, all have interesting properties; and cordierite has already found a special application. Its low coefficient of thermal expansion means that it does not fracture easily during rapid heating or cooling and thus finds use in refractories. In fact, it is the material used to form the honeycomb structure of catalytic converters.

The structures of beryl and cordierite are closely related. To change from one to the other, replace $3Be^{2+} + 2Al^{3+}(=12+)$ with $3Al^{3+} + 2Mg^{2+}(=13+)$. Then maintain overall neutrality by replacing one $Si^{4+}$ ion with an $Al^{3+}$ ion.

Tourmaline is quite complex, with one end member having the formula $NaAl_3Al_6B_3Si_6O_{30}(OH)$. The structure shown in Figure 7.8 is interesting because it exhibits trigonal, not hexagonal, symmetry. Because it is piezoelectric, tourmaline was used in the 1940s as a pressure-sensing component in the A-bomb. It is now used by some to "attract inspiration and to promote understanding."

**RING SILICATES**

| | |
|---|---|
| Beryl | $Be_3Al_2Si_6O_{18}$ |
| Cordierite | $Al_3Mg_2(Si_5Al)O_{18}$ |
| Tourmaline | $XY_3Z_6B_3Si_6(O,OH)_{30}(OH,F)$ |

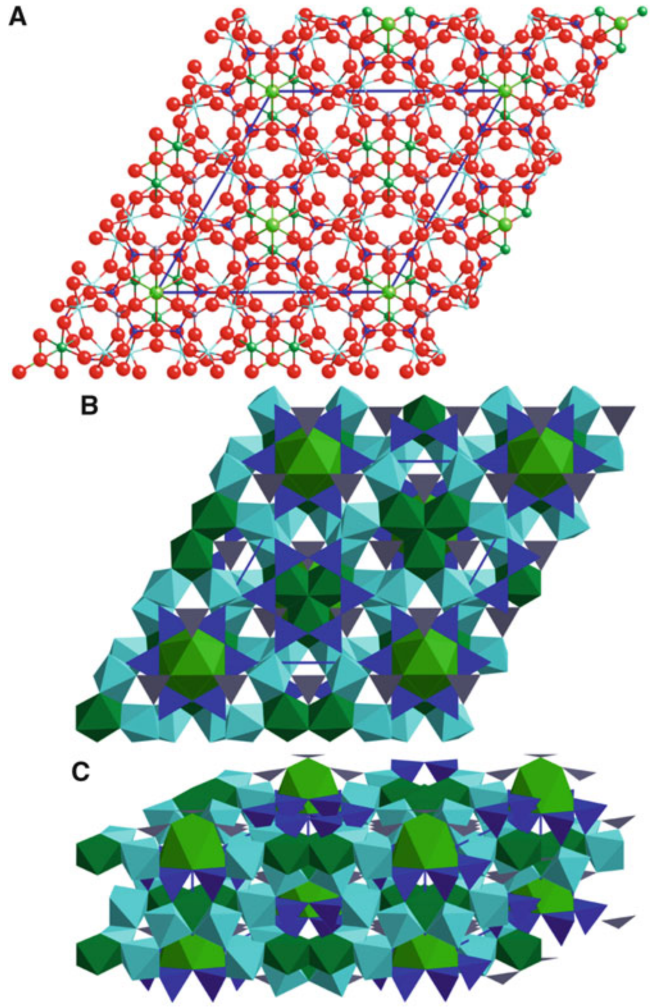


**FIGURE 7.8.** Crystal structure of tourmaline. The threefold axis can be seen. The lattice parameters are a = 1.58 and c = 0.71 nm. Most of the nominal 140 atoms in the cell sit in tetrahedral or octahedral sites, but the important boron ion sits at the center of three planar anions.

## 7.9 MICAS AND OTHER LAYER MATERIALS

Micas have very special properties: they are very rigid but cleave very easily along one plane. The crystal structure is well defined. The bonds within the layers are very strong, but those between the layers are weak; hence, they are known as layer materials. Before window glass was available, mica sheets were used as window material. We can easily cleave the sheets to produce a thin transparent ceramic.

Figure 7.9 shows the structure of mica. The van der Waals bonding between the sheets is not usually shown because it is so weak. Mica comes in several forms including muscovite, biotite, and the lesser-known phlogopite variety. Micas are used to provide easy paths for crack propagation in some commercial machinable ceramics.

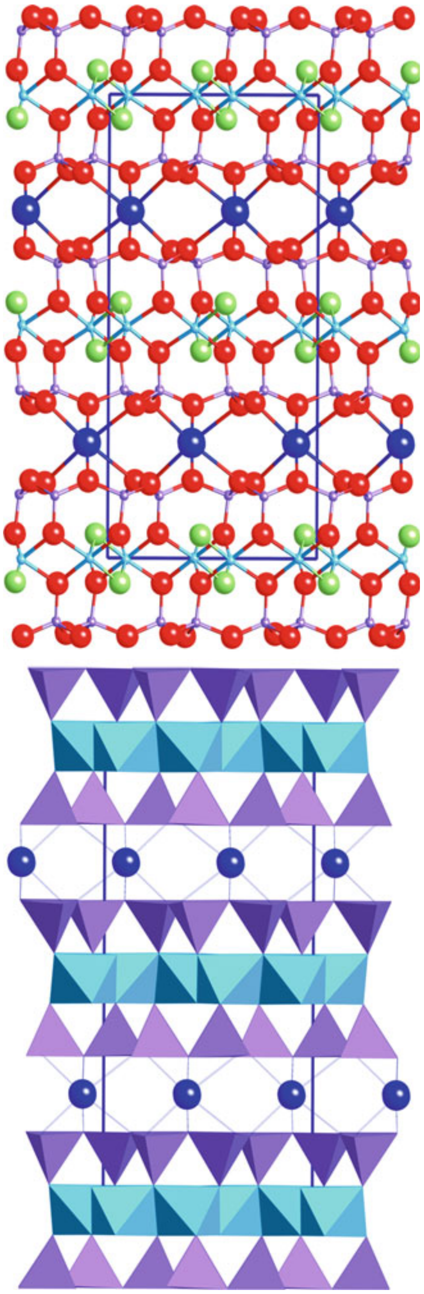


**FIGURE 7.9.** Crystal structure of mica showing the large $K^+$ ions forming a sheet of octahedral sites. The c lattice parameter normal to this sheet is 2.0 nm, with a and b being much smaller (0.52 and 0.90, respectively). The polyhedron model emphasizes the layer nature of the structure.

## 7.10 CLAY MINERALS

Clay minerals are among the most important materials we know or have ever known as they form the basis of pottery and building bricks. The properties of clays are determined by the fact that they are layer materials. They are a subgroup of the layer silicates. In general, the clay minerals are hydrated aluminum silicates based on $(Si_2O_5)_n$ sheets.

Kaolinite $[Al_2Si_2O_5\,(OH)_4]$ is the most common clay mineral. It is a 1:1 layer silicate, meaning that the structure

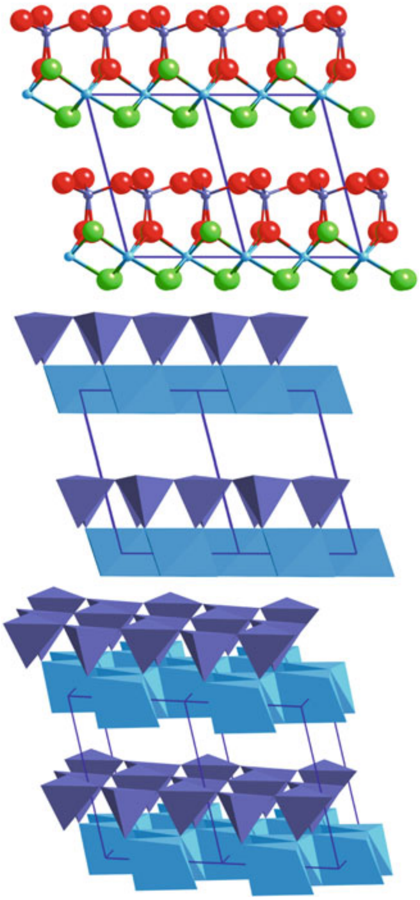


**FIGURE 7.10.** In the crystal structure of kaolinite, the $SiO_4$ tetrahedra form one side of the sheet, and the octahedra contain $OH^-$ on the outer layer attached to the $Al^{3+}$ ions. The sheets are held together only by van der Waals bonds.

consists of alternating layers of $[SiO_4]^{4-}$ tetrahedra combined with octahedrally coordinated aluminum ions, as shown schematically in Figure 7.10.

- In the tetrahedral sheet, each $[SiO_4]^{4-}$ tetrahedron shares three corners, forming a continuous sheet with the general formula $(Si_2O_5)_n^{2n-}$.
- The nonbonded tetrahedral apices of the sheet all point in the same direction.
- These apices connect the tetrahedral sheet to the octahedral sheet.
- The O atoms at the apex of each tetrahedron are shared with an octahedral sheet.
- The octahedral sheet is made up of an array of edge-sharing octahedra with either (OH) groups or O atoms at the corners.

**CLAY MINERAL GROUP**

Kaolinites
Smectites
Illites
Vermiculites

Because the charge must be balanced, $Al^{3+}$ ions occupy only two-thirds of the octahedral sites in kaolinite. The linkage between the tetrahedral and the octahedral sheets imposes restrictions on their relative sizes. If the fit between the sheets is not ideal, the resultant misfit leads to the formation of small crystals, as the strain imposed by any misfit increases with the area of the layer.

There is strong primary (covalent/ionic) bonding within each of the layers. However, the bonding between the layers is the weaker van der Waals type. Because the bonding is weak between the sheets, these silicates exhibit perfect one-directional cleavage.

Another member of the illite group is hydrous mica, where the principal interlayer cation is K. A smectite you might encounter is montmorillonite. Smectites can expand by incorporating water or organics between the structural layers. Vermiculite is derived from the Latin vermiculare, which means to breed worms and describes what appears to happen when the material is heated rapidly. Otherwise, it is very similar to phlogopite mica. As you would guess, most of these minerals have chemical compositions that are complex.

## 7.11 PYROXENE

The pyroxene group of minerals is a group of ferromagnesium silicates that occur in almost all types of igneous rock, so they are very important in mineralogy. Names you might encounter include enstatite, diopside, augite, jadeite, and spodumene; there are 20 accepted names of minerals in the group. The Si–O tetrahedra are linked at two corners and form an infinite chain parallel to the *z* axis. The base of each tetrahedron is nearly parallel to the (001) plane. The chains are then linked laterally by layers of octahedra, which contain six or eight coordinated cations such as Ca, Mg, Fe, or Na. The octahedra share edges and thus form continuous sheets on the (100) plane. A projection of the pyroxene structure in given in Figure 7.11.

| | | |
|---|---|---|
| Diopside | Monoclinic | $Ca(Mg,Fe)Si_2O_6$ ($a = 0.975$ nm, $b = 0.892$ nm, $c = 0.525$ nm, $\beta = 105.83°$) |
| Enstatite | Orthorhombic | $(Mg,Fe)_2Si_2O_6$ ($a = 1.822$ nm, $b = 0.881$ nm, $c = 0.517$ nm) |
| Jadeite | Monoclinic | $NaAlSi_2O_6$ |
| Spodumene | Monoclinic | $LiAlSi_2O_6$ |

You can guess the complexity of the structure from the lattice parameters! Although these materials are extremely important in mineralogy, they are not yet exploited much in ceramics.

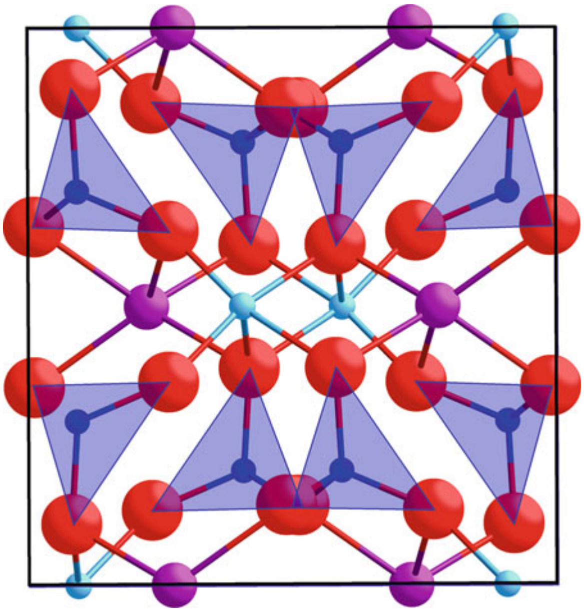


**FIGURE 7.11.** Crystal structure of a pyroxene (spodumene) shows layers of $Li^+$ (larger) and $Al^{3+}$ (smaller) ions in octahedra alternating with layers of $Si^{4+}$ in tetrahedra, giving a nominal formula of $LiAlSi_2O_6$.

## 7.12 β-ALUMINAS AND RELATED MATERIALS

The β-aluminas are a family of nonstoichiometric aluminates, the most important of which have the approximate formulae $Na_2O.11Al_2O_3$ (β-alumina), $Na_2O.8Al_2O_3$ (β′-alumina), and $Na_2O.5Al_2O_3$ (β″-alumina).

There are actually quite a few important ceramics that can be thought of as being constructed with layers of spinel separated by less-dense arrays of cations. These include not only the β-aluminas but also the magnetoplumbites and $CaAl_{12}O_{19}$ ($CA_6$: see Section 7.13). The model of the β-alumina structure is shown in Figure 7.12. We can think of this structure as being two twin-related blocks of spinel separated by a plane containing the large $Na^+$ ions. The result is that this "twin" plane is an open structure and that the c lattice parameter is large (2.12 nm for $CA_6$): it is a very anisotropic structure.

The $Na^+$ ions can move quite freely within the "twin" plane between the spinel layers; as a result the cation conductivity is high within these planes but negligible in the perpendicular direction. The high ion conductivity makes these ceramics of interest for battery applications, and this has been exploited in the Na-S cell. This cell was developed in ~1965 by Ford Motor Co. but has not been used in production. The main difficulty is that the cell must be kept at an operating temperature of 350°C to keep the electrode molten.

The mineral barium magnetoplumbite has the chemical formula $BaFe_{12}O_{19}$ or $BaO.6Fe_2O_3$ and is perhaps the most important of the hexagonal ferrites because it is a hard magnet with the spins all aligned along the *c* axis. This oxide is used in the magnetic stripe on credit cards.

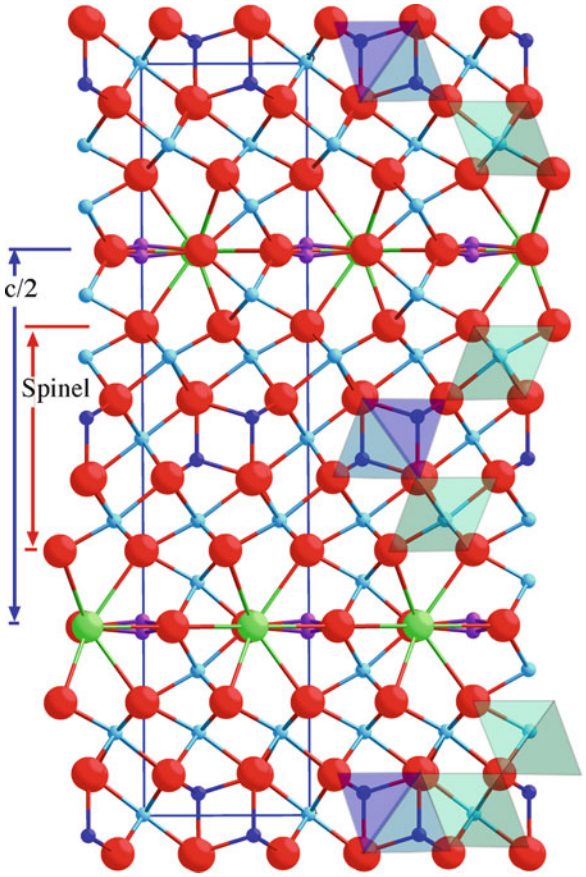


**FIGURE 7.12.** Crystal structure of β-alumina. The main features are the large value of c, the twinned spinel blocks, and the mirror plane containing the $Na^+$ (or $K^+$ or $Ca^+$) ion.

## 7.13 CALCIUM ALUMINATE AND RELATED MATERIALS

In Chapter 2 we mentioned cement and the reactions that occur during the setting and hardening of this material. There is a class of cements known as calcium aluminate cements (CACs) or high-alumina cements (HACs). These ceramics are not used as widely as Portland cement, but their attraction is the rapid hardening reactions. In 1 day CAC achieves the same strength as Portland cement achieves in a month.

The principal component present in CAC is calcium monoaluminate (CA in cement chemistry nomenclature; see Table 2.2). Its structure resembles that of β-tridymite, one of the polymorphs of $SiO_2$. Rather than having $[SiO_4]^{4-}$ tetrahedral sharing corners in CA, we have $[AlO_4]^{5-}$ tetrahedra. The large $Ca^{2+}$ ion distorts the tridymite network, and the structure is monoclinic.

The $[AlO_4]^{5-}$ tetrahedron is about the same size as the $[SiO_4]^{4-}$ tetrahedron and can form rings, chains, two-dimensional sheets, or three-dimensional networks in the same way by sharing oxygen corners. Other related calcium aluminates are also important in the chemistry of high alumina cements. The common feature of the structures of grossite ($CA_2$) and mayenite ($C_{12}A_7$) is that they too contain corner-sharing $AlO_4$ tetrahedra.

- Grossite, calcium dialuminate, is monoclinic. It is less reactive than CA.
- Mayenite, dodecacalcium hepta-aluminate, is cubic. It is the most reactive species in HACs.
- Hibonite, $CA_6$, is found in Ca-rich aluminas and has the magnetoplumbite structure (see Section 7.12).

## 7.14 MULLITE

Mullite is thought by some to be the most important ceramic although (like spinel) the name now refers to a group of ceramic materials. It is an orthorhombic silicate made up of chains of $AlO_6$ octahedra running parallel to the *z* axis and cross linked by tetrahedra containing Si and Al. In Figure 7.13 these chains of octahedra (Oc) are seen at the corners and center of the unit cell and run into the paper; the two parallel chains are rotated relative to one another. The polyhedron labeled C is not a tetrahedron, although it looks like one in this projection; T is a tetrahedron though. Sometimes the structure is rather different (it's a derivative), but the material is still called mullite (or a mullite). Mullite, the mineral, was originally from the Isle of Mull in Scotland and is $3Al_2O_3.2SiO_2$ or simply 3/2-mullite The composition actually varies over a wide range corresponding to $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$, quite a solid–solution range. The crystal structure can be related to that of sillimanite ($Al_2SiO_5$, i.e., $x = 0$ in the general formula or $Al_2O_3.SiO_2$) but is much more complicated! This causes problems when determining Burgers vectors of dislocations—the details of the crystal structure can be different in different mullites. $2Al_2O_3.2SiO_2$ has been produced synthetically. $Fe^{3+}$ and $Ti^{3+}$ can replace $Al^{3+}$—it's a very accommodating structure.

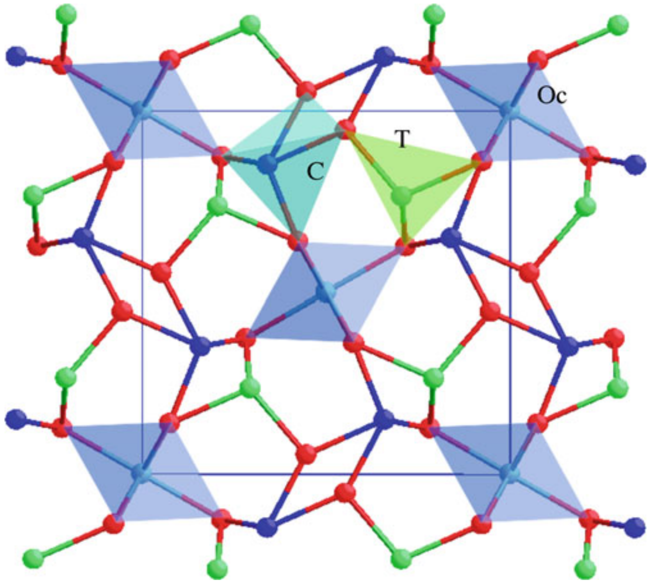


**FIGURE 7.13.** Crystal structure of mullite viewed along the short z axis (a = 0.76 nm, b = 0.77 nm, c = 0.29 nm). The sites Oc and T are never fully occupied, so this is an idealized schematic of this orthorhombic orthosilicate. The chains of octahedra at the corners and center lie along z.

Mullite has many important high-tech applications. We use mullite for coatings and for fibers. One use of mullite is in ceramic-matrix composites or CMCs; it has useful mechanical strength and has promise as the matrix for oxide reinforcing fibers. Above all, when we heat a clay containing $Al_2O_3$ and $SiO_2$, we form mullite—hence the claim that mullite is the most important ceramic and certainly the most important silicate for the ceramist.

## 7.15 MONAZITE

The mineral monazite has the composition $LnPO_4$; the anion is effectively $(PO_4)^{3-}$. In nature, the mineral actually consists of a mixture of several slightly different minerals because Ln (representing a lanthanide) can easily be replaced by one or more rare earths (Ce, La, Nd, etc.) and usually also contains thorium. There is some disagreement on the lattice parameters for monazite in the literature, which may in part depend on its purity. There are also two unit cells in use:

1. Monoclinic, $P2_1/n$, with $a = 0.6782$ nm, $b = 0.7057$ nm, $c = 0.6482$ nm, and $\beta = 103.21°$
2. Monoclinic, $P2_1/c$, with $a =$ same, $b =$ same, but $c = 0.6269$ nm ($a + c$ of "1") and $\beta = 126.53°$

The latter is correct by today's crystallographic conventions, but the former is found to be useful in describing defects such as twin boundaries. You may encounter both. Monazite is the primary ore for Th, Ce, and La; the first of these means that it is often radioactive. Mineral engineers have long known it as a principal source of Ce, but even then it often contains significant concentrations of $ThO_2$. Until the mid-1990s, few ceramists had heard of it. Then it was found to be a potential coating material for fibers to be used in ceramic composites. In this application, the composition chosen is usually $LaPO_4$.

## 7.16 $YBa_2Cu_3O_7$ AND RELATED HTSCs

$YBa_2Cu_3O_7$ (YBCO) has an orthorhombic layered-perovskite structure, with $c \sim 3a$ and $a \sim b$, as shown in Figure 7.14A. The Cu and O ions are arranged as chains along the *b*-direction between the Ba–O layers and as planes between the Ba-O and Y layers. Figure 7.14B shows how the YBCO structure is related to the perovskite structure. The structure consists of a sequence of oxide layers perpendicular to the c-axis as follows:

1. A Cu–O layer has two oxygen vacancies as compared with the "fully oxidized" YBCO perovskite. The Cu(1)

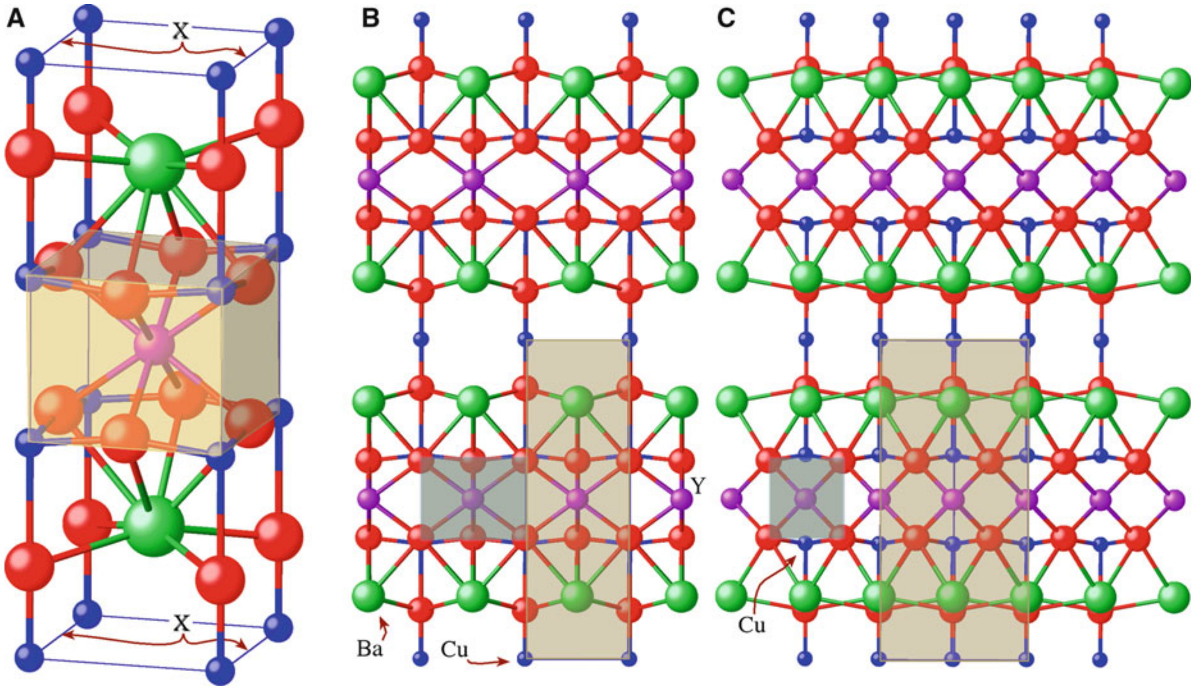


FIGURE 7.14. Models for YBCO. (A) Unit cell for the fully oxygenated compound (with . . .$O_7$); the shaded region shows the perovskite unit with Y in the center and Cu at the corners. (B, C) The structure is more readily appreciated from (B) [100] and (C) [110] views, each showing six unit cells. Note how the perovskite "unit cell" is rotated 45° relative to the unit cell of the YBCO.

site in this oxygen layer has CN $= 4$ and is surrounded by four oxygen ions in a square arrangement (as found in CuO). In $YBa_2Cu_3O_7$ this is the plane made by the CuO "chains."

2. A Ba–O layer.
3. A Cu–O layer in which the Cu(2) has a CN $= 5$ and is surrounded by five oxygen ions that form a square-based pyramid. This is the plane we call the $CuO_2$ plane.
4. A Y layer that has four oxygen vacancies as compared with the fully oxidized perovskite.

You can see in the literature that the chemical formula of YBCO is alternatively written as $YBa_2Cu_3O_{6+x}$ or $YBa_2Cu_3O_{7-\delta}$. The reason is that the material is almost always oxygen-deficient. So which form is correct? $YBa_2Cu_3O_6$ is an insulator. It has to be doped to gradually become a metallic-like conductor and a superconductor below $T_c$. The doping is achieved by adding additional oxygen-forming CuO "chains." These oxygen ions attract electrons from the $CuO_2$ planes that then become metallic. Thus, the "correct" formula for YBCO is $YBa_2Cu_3O_{6+x}$ where $x$ corresponds to partial oxygen content:

For $0.0 < x < 0.4$, $YBa_2Cu_3O_{6+x}$ is an insulator
For ~$0.4 < x < 1.0$, $YBa_2Cu_3O_{6+x}$ is a superconductor.

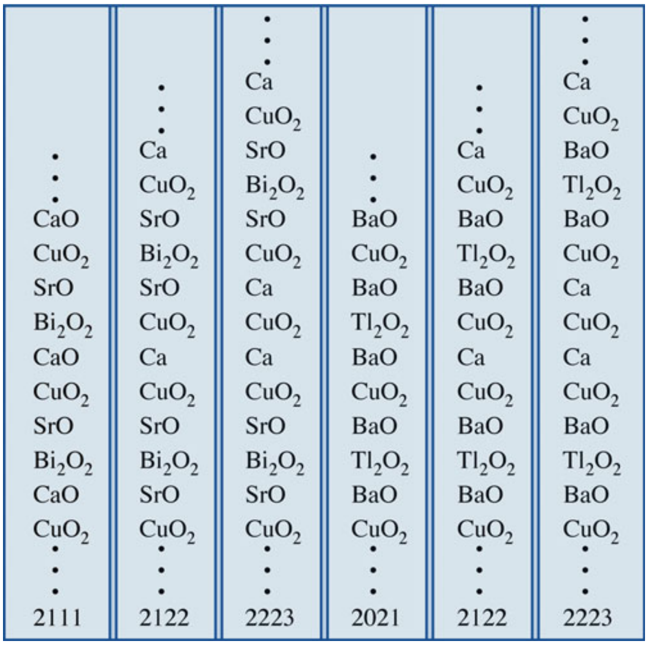
The oxygen content can be changed reversibly from 6.0 to 7.0 simply by pumping oxygen in and out of the parallel chains of CuO running along the $b$ axis. Careful studies indicate that the maximum $T_c$ is reached for $x \sim 0.93$ ($T_c = 94$ K) and that for $x = 1.0$ $T_c = 92$ K. (The important point is that liquid $N_2$ boils at 77 K).

It is thought that superconductivity essentially takes place within the quasi two-dimensional $CuO_2$ planes. The Cu–O chains can be considered as a "charge-reservoir" that is needed to transfer charge into the $CuO_2$ planes. This means we can consider this high-temperature superconductor (HTSC) as $CuO_2$ planes separated by a charge reservoir. Charge carriers are added by doping: adding oxygen to $YBa_2Cu_3O_6$, which enters the compound as $O^{2-}$ and forms CuO chains. To maintain charge balance, electrons are removed from the copper oxide planes, and the remaining holes are mobile (hence conduction). The properties are anisotropic (i.e., different along different directions). Therefore, orientation of the individual grains is essential in the fabrication of polycrystals or epitactic thin films.

The other HTSCs—bismuthates and thallates—are all layered structures with Cu–O planes present. The different phases are formed by stacking the same building-block layers in different sequences, as shown in Figure 7.15, producing, for example, $Bi_2Sr_2CaCu_2O_8$ (known as the Bi 2212 phase).

## 7.17 $Si_3N_4$, SiALONs, AND RELATED MATERIALS

Most of the materials discussed so far in this chapter have been oxides; and, in general, ceramists have neglected nonoxides. Part of the reason is that we often process



| | | | | | |
|---|---|---|---|---|---|
| | | ⋮ | | | ⋮ |
| | | Ca | | | Ca |
| | ⋮ | $CuO_2$ | | ⋮ | $CuO_2$ |
| | Ca | SrO | | Ca | BaO |
| ⋮ | $CuO_2$ | $Bi_2O_2$ | ⋮ | $CuO_2$ | $Tl_2O_2$ |
| CaO | SrO | SrO | BaO | BaO | BaO |
| $CuO_2$ | $Bi_2O_2$ | $CuO_2$ | $CuO_2$ | $Tl_2O_2$ | $CuO_2$ |
| SrO | SrO | Ca | BaO | BaO | Ca |
| $Bi_2O_2$ | $CuO_2$ | $CuO_2$ | $Tl_2O_2$ | $CuO_2$ | $CuO_2$ |
| CaO | Ca | Ca | BaO | Ca | Ca |
| $CuO_2$ | $CuO_2$ | $CuO_2$ | $CuO_2$ | $CuO_2$ | $CuO_2$ |
| SrO | SrO | SrO | BaO | BaO | BaO |
| $Bi_2O_2$ | $Bi_2O_2$ | $Bi_2O_2$ | $Tl_2O_2$ | $Tl_2O_2$ | $Tl_2O_2$ |
| CaO | SrO | SrO | BaO | BaO | BaO |
| $CuO_2$ | $CuO_2$ | $CuO_2$ | $CuO_2$ | $CuO_2$ | $CuO_2$ |
| ⋮ | ⋮ | ⋮ | ⋮ | ⋮ | ⋮ |
| 2111 | 2122 | 2223 | 2021 | 2122 | 2223 |

**FIGURE 7.15.** Different building-block layers that produce the Bi-phase oxide superconductors.

materials in a partial pressure of $O_2$. In what follows, we briefly introduce some of the exceptions that have not been mentioned previously.

Silicon nitride, $Si_3N_4$, exists in two forms, designated α and β. The structures and lattice parameters of these forms were determined by X-ray diffraction data.

$$\alpha\text{-}Si_3N_4;\ \text{hexagonal}: a = 0.7748\ \text{nm};\ c = 0.5617\ \text{nm}.$$
$$\text{Space group P}6_3/\text{m}$$
$$\beta\text{-}Si_3N_4;\ \text{hexagonal}: a = 0.7608\ \text{nm};\ c = 0.29107\ \text{nm}.$$
$$\text{Space group P31c}$$

Each Si is at the center of a slightly irregular tetrahedron of nitrogen atoms. The $SiN_4$ units then share corners; each N is common to three tetrahedra. The structures differ in the arrangement of the tetrahedral units. Planes of atoms in the β form are linked along the [001] direction in a sequence ABAB. . ., whereas in the α form the sequence is ABCDABCD. . ..

The $SiN_4$ and $SiO_4$ tetrahedra are similar, except that whereas each oxygen atom in $SiO_4$ is common to two tetrahedra, each nitrogen atom in $SiN_4$ is common to three tetrahedra.

By substituting $O^{2-}$ for $N^{3-}$ and $Al^{3+}$ for $Si^{4+}$ we can form a family of compounds known as "SiAlONs." They can be produced by high-temperature reactions between, for example, $Si_3N_4$ and $Al_2O_3$. The general formula for the SiAlONs is $(Si,Al)_3(O,N)_4$. Other metal atoms can be incorporated into the structure giving $(Si,M)(O,N)_4$; possibilities for M include Mg + Al, Li + Al, and Y.

*Other nitrides.* The interest in $\beta$-$C_3N_4$ is that it is predicted to have a bulk elastic modulus comparable to diamond. Several attempts have been made, with varying degrees of success, to produce it in bulk and as a thin film. The structure of $\beta$-$C_3N_4$ is related to the $\beta$-$Si_3N_4$ structure. The $CN_4$ tetrahedra link by sharing N atoms. Each C atom has four nearest neighbors, forming an almost regular tetrahedron; and each N has three nearest-neighbor C atoms, forming 120° bond angles.

## 7.18 FULLERENES AND NANOTUBES

In Chapter 6, we discussed the structure of diamond and graphite—allotropes of carbon. The discovery of the $C_{60}$ molecule in 1985 introduced a new, third, ordered form of carbon—the fullerenes. The special new feature of $C_{60}$ (shown in Figure 7.16A) is the regular incorporation of five-sided rings of C atoms that allow the formation of curved sheets of carbon atoms. $C_{60}$ has 12 pentagonal (five-sided) and 20 hexagonal (six-sided) faces symmetrically arrayed to form a molecular ball; in fact, a soccer ball uses the same geometric configuration as fullerene.

In the solid state, the $C_{60}$ molecules bind with each other through weak van der Waals forces and can self-assemble to form an fcc arrangement. At room temperature, the size of the cubic unit cell is 1.4 nm, and the nearest-neighbor $C_{60}$–$C_{60}$ distance is 1.0 nm. At lower temperatures, the arrangement of the fullerenes may become simple cubic with a larger unit cell. In the fcc arrangements there are, of course, intersticies with either octahedral or tetrahedral character. Alkali metal atoms such as K or Rb can be incorporated into the interstitial sites to give a molecular formula of $K_3C_{60}$ or $Rb_3C_{60}$. The interest in these doped fullerenes is that they are superconductors. The highest $T_c$ in the series of alkali metal doped $C_{60}$ is 33 K for $Cs_2RbC_{60}$.

A wide variety of fullerene structures have been produced with the general formula $C_n$, where $n$ can take on small (70) or very large (240 and 540) values. In each case, the structure consists of 12 uniformly distributed pentagons connecting an array of hexagons.

Although pentagons are necessary to give an approximately spherical shape, by simply rolling a hexagonal graphite sheet we can produce carbon nanotubes. These objects can be considered a new source of mesoporous ceramics. They are dimensionally confined in two directions. If the ends are closed, as shown in Figure 7.16B, we again need to incorporate the pentagon. Just as graphite grows as sheets, the single-walled nanotube (SWNT) can grow as a multi-walled nanotube as you can see in Figure 7.16C. The "layer" spacing of the walls is usually what we expect from graphite except at the closed ends. It is an interesting exercise to take a single sheet of graphite (drawn on paper), roll it, and rejoin the bonds; you immediately realize that you can introduce a shear or chirality

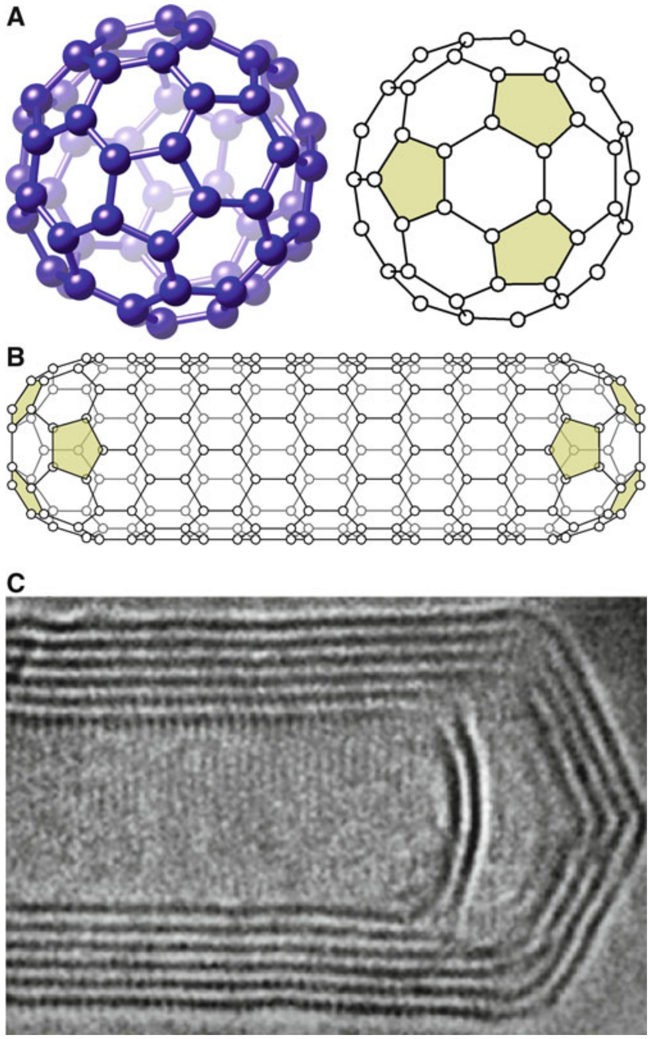


**FIGURE 7.16.** The structure of (a) $C_{60}$ and (b) carbon nanotubes. (c) Image of the end of a six-layer carbon nanotube.

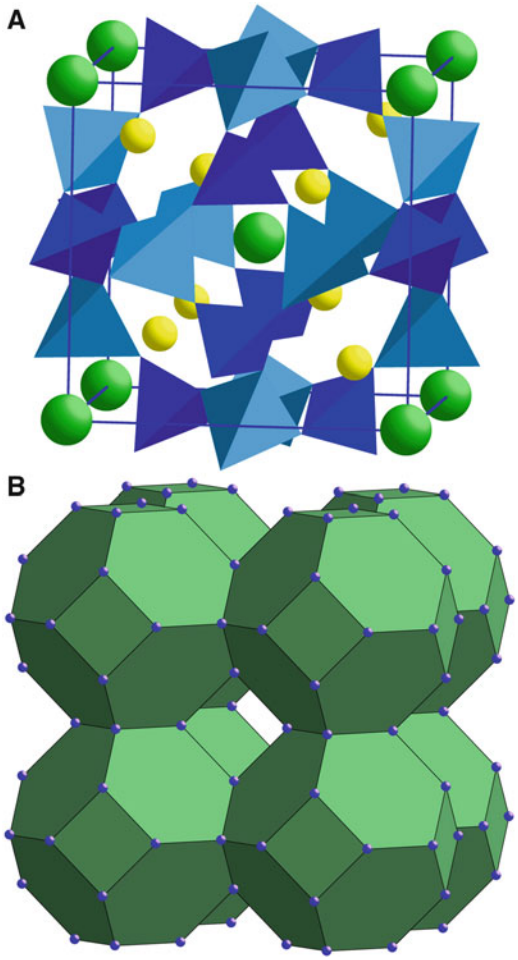


**FIGURE 7.17.** Structure of sodalite, a zeolite. The tetrahedra shown in "a" link together to form large "cages." The most important features are the channels between the cages, which are seen in "b." In "a" the corner and body centering ions are $Cl^-$; the others are $Na^+$ ions. The tetrahedra contain either $Si^+$ or $Al^+$.

(like a screw dislocation along the tube). The chirality determines the electrical conduction along the nanotube.

Many variations on the C nanotube can be produced using other layer materials such as $MoS_2$. Tubes built from other oxides that are not layer materials might sometimes be better described as pipes.

## 7.19 ZEOLITES AND MICROPOROUS COMPOUNDS

Zeolites are aluminosilicates that have a framework structure with large cavities built in. The general formula of the zeolites is $(Na_2,K_2,Ca,Ba)[(Al,Si)O_2]_n.xH_2O$, which means that they are chemically related to the feldspars. They are found in nature as crystals with large mineral specimens coming from Pune (near Mumbai in India). They are becoming much more important as synthetic minerals when they are used as molecular sieves or catalyst supports. The atlas of zeolite types lists 98 tetrahedral frameworks that are structurally distinct and are known as the TO4 frameworks, where T (at the center of the O tetrahedron) is usually either Si or Al but could be P, Ga, B, or other components. The International Zeolite Association (IZA) has compiled the different structural types and given each one a three-letter code, which they call the Structural Type Code. The 3D frameworks are then assembled using secondary building units (SBUs) that consist of 4, 5, and 6-rings. You can appreciate the idea by examining the example shown in Figure 7.17. This figure represents sodalite, which is actually cubic with a lattice parameter of 0.887 nm.

Microporous ceramics are being designed to extend the concept of zeolites by building structures that do not necessarily have the well-defined walls of a zeolite crystal but still have the large cavities; an ordered alignment of the cavities can make it appear that the material is crystalline. The IUPAC definition is that a microporous material contains micropores (free diameter $<2$ nm); mesoporous materials contain mesopores (free diameter 2–50 nm).

## 7.20 ZACHARIASEN'S RULES FOR THE STRUCTURE OF GLASS

Many compounds can form glasses. Silicate glasses are what we usually think of as "glass." However, the topic actually includes many other materials that are thought of as amorphous; but even that terminology can be misleading. In this section, we just discuss the aspects of structure as they relate to the theme of polyhedra. We leave the question of "what is a glass?" to Chapter 21.

In 1932, W.H. Zachariasen proposed a set of rules that are usually satisfied when an oxide forms a glass. His analysis was based on the following considerations:

1. The interatomic bonding forces in glasses and crystals must be similar given the similar elastic modulus of the two types of solids.
2. Like crystals, glasses consist of an extended 3D network, but the network does not have translational periodicity.

Studying the structure of glass is difficult because of the lack of translational symmetry. X-ray diffraction spectra from glasses show diffuse maxima, not sharp spots or even sharp rings. These diffuse rings can be interpreted in terms of a radial distribution function (RDF is the acronym; the quantity is $\rho(\mathbf{r})$).

$\rho(\mathbf{r})$ = atom density in a spherical shell of radius $r$ from the center of any selected atom.

An illustration of such a function is shown in Figure 7.18. The peaks in this figure correspond to the broad bands seen in the diffraction pattern. The corresponding plot for the crystalline material is also shown. The function is equally applicable for a crystal, but the peaks are then delta functions. What is less clear is whether or not a particular (or any) glass is truly amorphous or if "crystallites" at the nanometer scale are present.

The structure of an oxide glass can be modeled in terms of coordination polyhedra of cations surrounded by a variable number of oxygen ions. In crystalline oxides, the polyhedra can share not only corners but also edges and/or faces; in glasses the polyhedra can share only corners. Silica glass is then pictured as a disordered version of the crystal with all oxygen ions bridging terahedra, as shown in Figure 7.19.

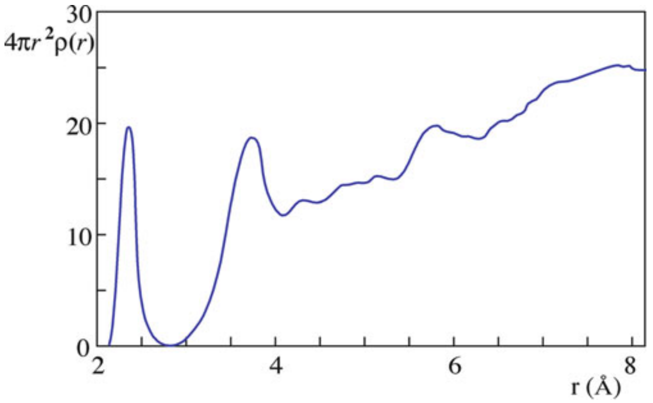


**FIGURE 7.18.** Radial distribution function of a glass showing a sharp first-neighbor peak, a broader second-neighbor peak, and then a gradual increase with increasing *r*.

Zachariasen summarized his findings as four rules and emphasized how the structure of $SiO_2$ glass differs from the crystalline form shown here as the (111) plane of cristobalite.

1. An oxygen ion links to two or fewer glass-forming atoms.
2. CN of the glass-forming atoms is small.
3. Oxygen polyhedra share only corners.
4. Polyhedra form a 3D network.

These rules have been used since the 1930s and have become almost folklore. You should remember that they were proposed when the main glasses studied were silicates, although borate and phosphate glasses were known.

Further tendencies for glass formers have been listed.

1. The valence of the cation is ≥3.
2. As the size of the cation decreases, so does its glass-forming tendency.
3. The cation's electronegativity is between 1.5 and 2.5.

In a general way, the role of the cations depends on the valence, CN, and the related values of the single-bond strength. Cations of higher valence and lower coordination than the alkalis and alkaline earth oxides may also

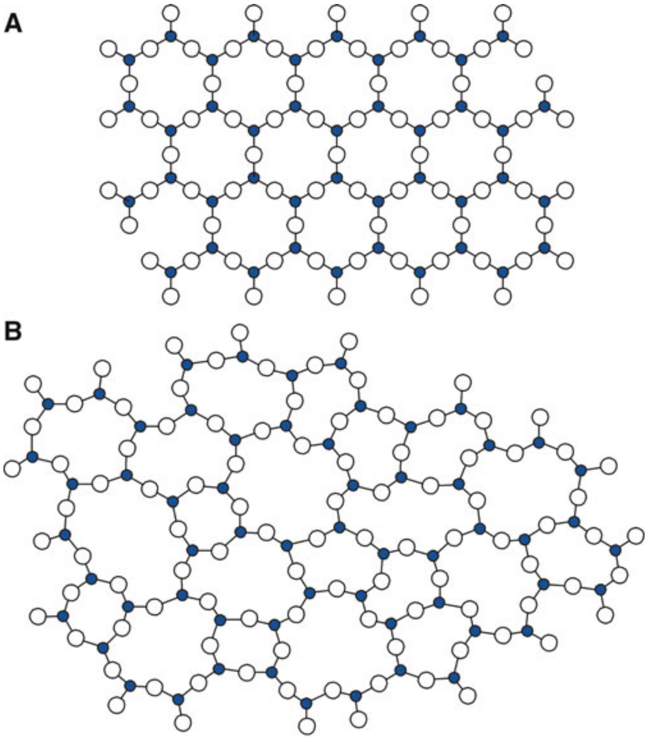


**FIGURE 7.19.** Comparing the structures of (a) crystalline silica and (b) glass.

TABLE 7.7 CN for Formers, Modifiers, and Intermediates

| **Formers** | | **Intermediates** | | **Modifiers** | |
|---|---|---|---|---|---|
| *Ion* | *CN* | *Ion* | *CN* | *Ion* | *CN* |
| Si | 4 | | | Li | 1 |
| Ge | 4 | | | Na | 1 |
| B | 3 | | | K | 1 |
| Al | 3 | Al | 3 | Cs | 1 |
| P | 5 | | | Rb | 1 |
| V | 5 | Be | 2 | Be | 2 |
| As | 5 | | | Mg | 2 |
| Sb | 5 | | | Ca | 2 |
| Zr | 4 | Zr | 4 | Ba | 2 |
| | | | | Sr | 2 |
| | | Zn | 2 | Zn | 2 |
| | | Cd | 2 | Cd | 2 |
| | | | | Hg | 2 |
| | | | | Ga | 3 |
| | | | | Sn | 4 |
| | | Pb | 2 | Pb | 4 |

contribute in part to the network structure. We can list the cations in three groups. The different types of ion present in oxide glasses are summarized in Table 7.7.

1. Network formers are those cations that form coordination polyhedra in glass (e.g., Si).
2. Network modifiers are those oxides that do not participate directly in the network (e.g., Na).
3. Intermediate ions can sometimes act in either role (e.g., Al).

In practice, in oxide glasses the polyhedra are triangles and tetrahedra. When a network modifier such as $Na_2O$ is added to silica glass ($SiO_2$), a specific number of Si–O bonds are broken. This process is represented schematically in Figure 7.20. Si–O bonds are broken, and the added oxygen saturates the unsatisfied bond of one Si; and two Si–$O^-$ bonds are formed. The excess negative charge on the oxygen is compensated by the nearby $Na^+$ cations (adding an ionic character to the glass). The Si–O–Si bridge-rupture mechanism leads to a loosened network structure with two types of oxygen:

1. Bridging oxygens are bonded to two Si.
2. Nonbridging oxygens (NBOs) are bonded to one Si.

To summarize, Zachariasen's model has dominated glass science for several decades and is still extremely useful. However, diffraction methods do not actually provide definitive proof for such a model; they can only confirm that the results do not contradict this hypothesis. Remember also that the model was developed specifically for oxide glasses and is not necessarily applicable to other types of glasses.

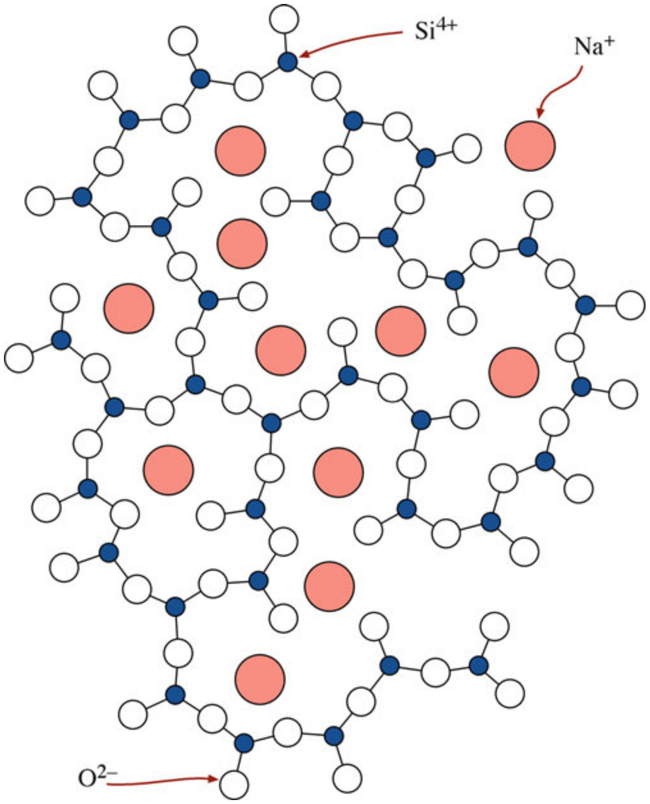


**FIGURE 7.20.** How network modifiers in glass cause nonbridging O ions.

## 7.21 REVISITING GLASS STRUCTURES

The Zachariasen model began to be reexamined in the 1990s. The important point is that silicate glass is, in many ways, just like the other silicates that *do* have long-range order. Most especially they are all 3D solids. Figure 7.21 shows the same information as in Figure 7.19B, but it is redrawn to show different ways of looking at this structure. A crystal composed of corner-sharing $SiO_4$ tetrahedra (Figure 7.21A) has orientational and translational symmetry. We can then call such a network "topologically ordered." A silica glass is then topologically disordered—we can't describe it by symmetry operations, but it looks very similar to the crystalline form otherwise. The tetrahedron is an example of a rigid structuring element called a polytope (i.e., our polyhedra). The connectivity of a 3D structure can be described by the parameter $\{V, C\}$, where $V$ is the number of vertices per polytope, and $C$ is the number of polytopes sharing a vertex. Incidentally, the polytope for the glass former $B_2O_3$ is the $BO_3$ triangle, so the tetrahedron is not the essential polytope. A network of triangles on a plane joining at the vertices is a {3,2} arrangement.

For our ($SiO_4$) tetrahedron $V$ is 4, but the diagram shown in Figure 7.19B is actually a two-dimensional continuous random network of triangular polytopes. with $V = 3$ and $C = 2$ (so it's {3,2}). The Si atoms

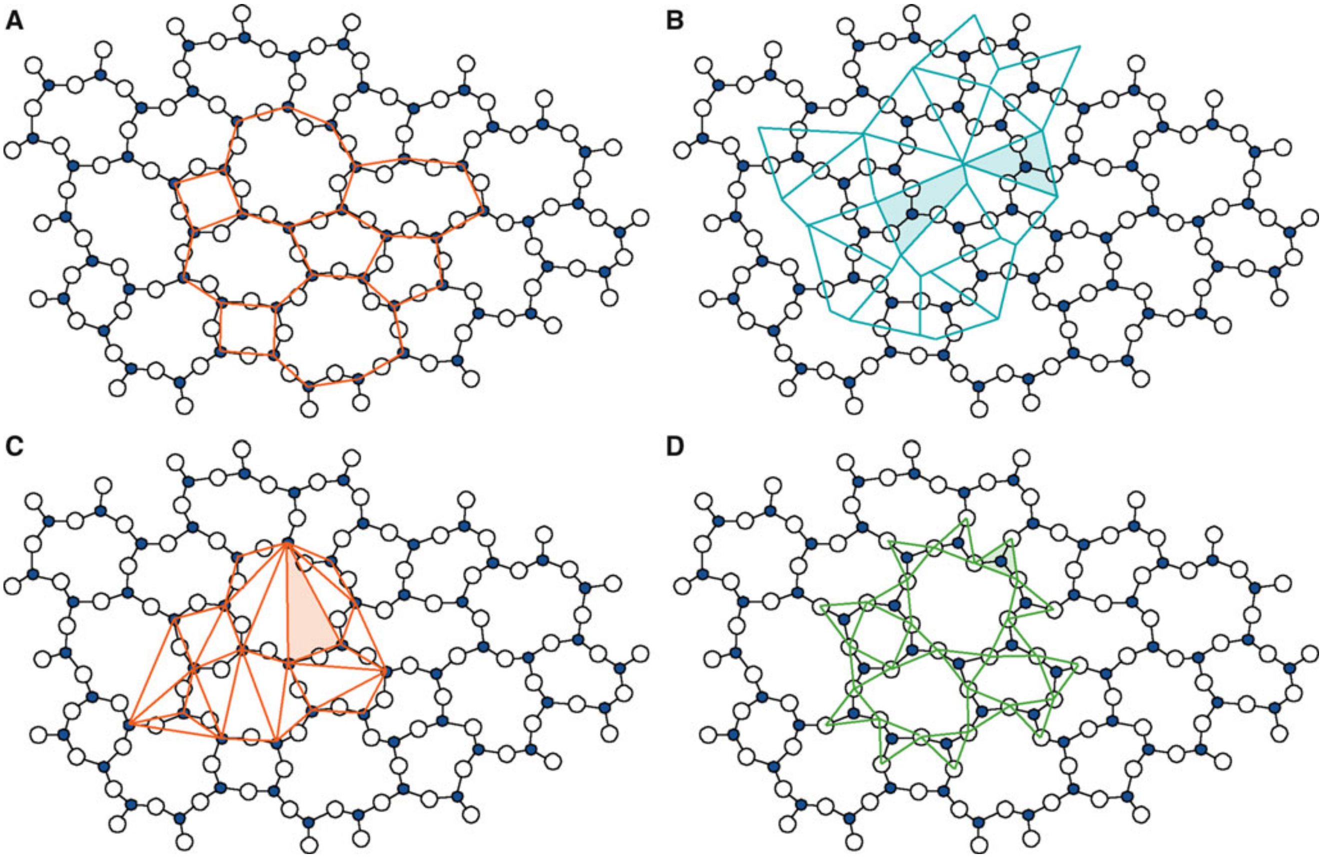


**FIGURE 7.21.** Different ways of representing the same array of ions in a silica glass.

define a point (which can be called a node) in each triangle. If we join these nodes as in Figure 7.21A, then we have an array of primitive rings; now this network of nodes is a {2,3} set because we're just joining lines, and three join at each junction. This new network is said to tile or tessellate the two-dimensional space. The set of tetrahedra associated with this ring is then called a local cluster and can be compared to the unit cell in a crystal. Alternative tiling schemes are shown in Figure 7.21B, C. The challenge is to describe the 3D structure. Our usual way of looking at it is shown in Figure 7.21D.

## CHAPTER SUMMARY

This chapter examined some crystals structures that students must learn, including spinel and perovskite. Students should also know the different arrangements of the $SiO_4$ tetrahedra. Most of the other structures are looked up as needed, but the idea of how to build micas and clays really should be known. The structures of materials such as the β-aluminas, YBCO, the SiAlONs, and the fullerenes all use concepts that we examined in Chapter 6 but in a more complicated form. The special feature in the fullerenes is the five-sided ring; in Chapters 12 and 14 we'll see five-sided rings in dislocation cores and grain boundaries in Si and Ge, where they have been known since before 1960. These structural features were well known years before they were discovered. You can look up the complex structures, but you should be able to recognize the special features of each one and how they are constructed from simple atomic groupings. Zeolites are endlessly fascinating and are like enormous 3D crossword puzzles. These materials are often left to inorganic chemists to synthesize or chemical engineers to use, which is unfortunate because their applications in materials science and engineering are far-reaching. Two pages on glass is not adequate treatment but hopefully shows you some of the potential for discovery in these noncrystalline solids.

## PEOPLE AND HISTORY

*Curl, Robert F. Jr.* (1933–), *Richard E. Smalley* (1943–2005), and *Sir Harold W. Kroto* (1939–). These men shared the 1996 Nobel Prize in Chemistry for their discovery of fullerenes. In 1999, buckyballs were found to exist naturally in a meteor.

*Fuller, Richard Buckminster* (1895–1983). He was an architect and inventor of the geodesic dome that resembles the structure of $C_{60}$, shown in Figure 7.16A. $C_{60}$ is often t referred to as the buckyball.

*Megaw, Helen Dick.* She died in 2002 at age 94. She reported the crystal structure of $BaTiO_3$ in *Nature* (155:484, 1945). She spent most of her academic career in Cambridge.

*Zachariasen, William Houlder* (1906–1980). This Norwegian-American physicist spent most of his career working in X-ray crystallography, but he is best remembered for his description of the glass structure in the early 1930s. He wrote only one paper on glass and was surprised to see it become the work that he is remembered for (information courtesy Jim Philips).

## EXERCISES

7.1 Compare the ionic sizes in $CaZrO_4$ and $CaSiO_4$ and discuss how well they fit Pauling's rules and if they should.

7.2 Discuss for $Mg_2TiO_4$ and Mn-Zn ferrite, which is preferred, normal or inverse spinel, on the basis of Pauling's rules.

7.3 In spinel, other than $<110>$, is there a low-index direction where only like cations project on one another?

7.4 How many ions do you expect to find in a unit cell of grossular?

7.5 Discuss whether we should write the formula for superconducting YBCO as $YBa_2Cu_3O_{7-\delta}$ or $YBa_2Cu_3O_{6+x}$.

7.6 We often say that the structure of YBCO is related to the perovskite structure. Draw diagrams of the two crystal structures and then explain this relation.

7.7 By delving into the literature, explain which three ceramic materials you think are the next (after those discussed in the chapter) most important in each of these categories: silicates, oxides, nonoxides. Then summarize how they are processed.

7.8 In silicon oxynitride, $Si_2N_2O$, we have $SiN_3O$ tetrahedra. Sketch the possible structure of this ceramic.

7.9 Consider the fcc arrangement of doped solid $C_{60}$ that we described in Section 7.18. Explain why we get only $Cs_1C_{60}$ when we dope with Cs and why for sodium doping we can get $Na_6C_{60}$ and $Na_{10}C_{60}$.

7.10 By examining the literature, discuss how niobates and titanates can be combined and how the perovskite structure facilitates it.

7.11 Using Table 7.1, comment on $r_M$ for the following groups of ions: (a) $Li^+$, $Na^+$, $K^+$; (b) $Si^{4+}$, $Ge^{4+}$, $Ce^{4+}$, $Zr^{4+}$; (c) $B^{3+}$, $Al^{3+}$.

7.12 If maghemite and magnetite both have the spinel structure, how can this be if spinel is $AB_2O_4$?

7.13 Label three planes for both Figure 7.1B and C.

7.14 Knowing the structure and lattice parameters of $BaTiO_3$, deduce the lattice parameters of $CaTiO_3$.

7.15 $CaTiO_3$ is the mineral perovskite. Why is $BaTiO_3$ much more important (explain the effect of Ba rather than Ca)? How does $SrTiO_3$ fit into your scheme?

7.16 Add another two silicates to each of the columns in Figure 7.4. Reference your sources.

7.17 The silicates in Table 7.3 are not just catalog items for mineralogists. Use the literature to find one commercial use for each one listed.

7.18 In Table 7.7 Al is listed as a former and an intermediate and Pb as an intermediate and a modifier. Under what conditions do you think Pb might be an intermediate and under what conditions do you think Pb might act as a modifier? Do you think the location of the Pb would affect lead release from Pb-containing glasses?

7.19 Tourmaline was very important in the period 1945–1955. What has replaced it, and why did it "work" so well when it was used.

7.20 The β-aluminas have potential applications for batteries. Discuss the different structures of the β-aluminas, how you would measure their conductivity, and what you would use to store the charge.

## REFERENCES

In addition to the references given in chapter 6, the following are recommended.

## GENERAL REFERENCES

Baerlocher Ch, Meier WM, Olson DH (2001) Atlas of zeolite framework types, 5E. Elsevier, Amsterdam. Requires a good understanding of crystallography but lots of sources for future exploration. You can download the atlas from the site for the *International Zeolite Association*. http://www.iza-structure.org/databases

Deer WA, Howie RA, Zussman J (1992) An introduction to the rock-forming minerals, 2nd edn. Longman, London, This book (680+ pages) contains a wealth of data on the subject. Olivines, garnets and pyroxenes abound

Doremus RH (1994) Glass science, 2nd edn. Wiley, New York, This is the first book to go to when you continue your study of glass

Griffen DT (1992) Silicate crystal chemistry. Oxford University Press, Oxford, Clear diagrams but doesn't include mullite

Hobbs LW (1995) The role of topology and geometry in the irradiation-induced amorphization of network structures. J Non-Cryst Solids 182:27–39, Polyhedra as polytopes and much, much more

Hobbs LW, Jesurum CE, Pulim V, Berger B (1998) Local topology of silica networks. Philos Mag A78:679–711

Liebau F (1985) Structural chemistry of silicates. Springer, Berlin, Great reading but not easy

Melody (1995) Love is in the earth: a kaleidoscope of crystals. Earth-Love, Wheat Ridge, If you are interested in an entirely different assessment of ceramics! 16th printing in 2003

Parthé E (1964) Crystal chemistry of tetrahedral structures. Gordon and Breach, New York, Chapter IV and Appendix A

Schneider H, Komarneni S (eds) (2006) Mullite. Wiley, Weinheim, The definitive library book on this important group, though structurally complex, of materials

Sosman RB (1965) The phases of silica. Rutgers University Press, New Brunswick, The classic, though now a little neglected, text on silica

Stanworth JE (1971) Oxide glass formation from the melt. J Am Ceram Soc 54:61–63

Wells AF (1984) Structural inorganic chemistry, 5th edn. Oxford University Press, Oxford, Repeated here because this book is so important

Wenk H-R, Bilakh A (2004) Minerals their constitution and origin. Cambridge University Press, Cambridge, Concentrates on the materials—a super resource

## SPECIFIC REFERENCES

Fenner CN (1913) The stability relations of the silica minerals. Am J Sci 36:331–384, Gave the original version of the silica phase diagram

Hardie D, Jack KH (1957) Crystal structures of silicon nitride. Nature 180:332, Initial report of the structures of $Si_3N_4$

Hay RS, Marshall DB (2003) Deformation twinning in monazite. Acta Mater 51:5235–5254, and Hahn T, ed., *Space Group Symmetry*. International Tables for Crystallography, Brief Teaching Ed., (D. Reidel Pub. Co., Dordrecht) 1985

Jack KH (1976) SiAlONs and related nitrogen ceramics. J Mater Sci 11:1135, A review article by the pioneer in the field. The most cited article in *Journal of Materials Science*

Liu AY, Cohen ML (1989) Predication of new low compressibility solids. Science 245:841, Proposes a compound $\beta$-$C_3N_4$, which should have outstanding mechanical properties but it is not widely available (it's very rare). This paper has over 1200 citations

Zachariasen WH (1932) The atomic arrangement in glass. J Am Chem Soc 54:3841, The random network model for glass structure has been the dominant factor in developing glass formulations for 70 years. This is the classic reference for that model