

5

Models, Crystals, and Chemistry

CHAPTER PREVIEW

Most ceramics are crystalline. The exception is glass, which we usually discuss separately. Not only do the properties of ceramic crystals depend on how the atoms or ions are arranged, but the type and nature of defects also depend on crystal structure. You probably first encountered crystallography when discussing metals. Sixty-five (almost 90%) of the metallic elements are either cubic or hexagonal. In ceramics, many of the most important materials are neither cubic nor hexagonal, so we need to be more familiar with the rest of the subject. It is recommended that you memorize the main structures described in Chapters 6 and 7. In this chapter we provide the means to make this study more systematic.

To understand why ceramics have particular structures and why certain defects form in these structures, it is really important to understand Pauling's rules. These rules require you to visualize a tetrahedron and an octahedron and to see how they fit together. To understand properties such as piezoelectricity or the mechanisms of phase transformations, you must be able to visualize the crystal structure of the material. This is particularly important when we want to predict the properties of single crystals. We summarize the features of crystallography that we use throughout the text and give references to more specialized resources for rigorous proof of theorems and more detailed discussion.

An important point to keep in mind is that the term "ceramic" generally refers to materials that have been processed in the laboratory or the factory plant but that often do exist in nature. Sometimes the natural minerals are rare such as moissanite, which is now being manufactured as a gemstone. There are far more materials and structures in nature than are used in technology. Understanding the basic principles and knowing where to learn more about minerals may help you find the next monazite or at least to know why it might be useful. A great source for further reading lies in the mineralogical literature.

5.1 TERMS AND DEFINITIONS

We will begin by defining the vocabulary of the subject. Most of this section should be familiar to you from other courses.

Crystal Lattice: A three-dimensional array of points related by translational symmetry. The translation can occur in three independent directions giving three independent base vectors. We can fully describe such a lattice by three vectors, **a**, **b**, **c**, and three angles, α , β , γ . The special property of a crystal lattice is that the lattice points are identical: if we have an atom at or near one point, there must be an identical atom at the same position relative to every other lattice point.

Unit Cell: The vectors **a**, **b**, **c** define a cell. There is, in principle, an infinite number of ways to define a unit cell in any crystal lattice. But, as in many areas of crystallography, there is a convention:

1. The unit cell should have the same symmetry as the crystal—the base vectors are parallel to symmetry axes or perpendicular to symmetry planes.
2. The origin of the unit cell is usually a center of symmetry.
3. The base vectors should be as short as possible and the cell volume should be as small as possible. The exceptions arise when choosing a longer vector and a larger cell makes the symmetry more obvious.
4. The angles between the axes should be as close as possible to 90° , or if not then $>90^\circ$.
5. A unit cell having the smallest possible volume is called a primitive cell.

Lattice Parameters: The vectors **a**, **b**, **c** and the angles α , β , γ are called the lattice parameters of the unit cell. Tabulated lattice parameters are, unless otherwise stated, values at room temperature and pressure. They vary with changes in temperature or pressure.

Crystal System: There are seven unique shapes that can each be used to fill three-dimensional space.

These are the seven crystal systems into which all crystals are classified. They are listed in order of increasing symmetry in Table 5.1.

Bravais Lattices: There are 14 different ways to arrange lattice points. These are constructed as three separate types:

- Primitive (P) lattices—one lattice point per unit cell
- Body-centered (I) lattices—a lattice point at the corners and one in the center of the cell
- A-, B-, C-, or F-centered lattices—a lattice point at the corners and others at one (A, B, C) or all three (F) of the faces

The 14 Bravais lattices are shown in Figure 5.1. For reasons of symmetry (Rule 1 above) we do not always choose a primitive cell. The face-centered cubic cell may be referred to the rhombohedral cell (which is primitive), but the cubic cell reflects the higher symmetry of the lattice.

Lattice Points Per Cell: Primitive cells have only one lattice point per cell whereas nonprimitive cells have more than one. A lattice point in the interior of a cell (N_i) can be thought of as belonging entirely to that cell; one in a cell face (N_f) is shared by two cells and a corner one (N_c) is shared by eight. The number of lattice points (N) per cell is given by

CRYSTAL SYSTEMS
All crystals belong to one of the seven crystal systems.

$$N = N_i + \frac{N_f}{2} + \frac{N_c}{8} \quad (5.1)$$

Basis: Group of atoms associated with each and every lattice point. We can describe crystal structures in terms of a Bravais lattice and a Basis:

$$\text{Bravais Lattice} + \text{Basis} = \text{Crystal Structure} \quad (5.2)$$

This approach is often used by solid-state physicists and is particularly useful when we want to determine the structure factor of a crystal. Crystal structures are formed by placing a basis of atoms either on the points of a Bravais lattice or in some fixed relation to those points. There may be no atoms actually located on the lattice points.

Coordination Number (CN): Number of nearest neighbors.

Symmetry Elements: These symmetry elements are easy to understand because you can see them by handling real crystals or crystal shapes. For example, crystals of MgO are cubic and calcite (CaCO_3) is trigonal as shown in Figure 5.2. They apply to macroscopic shapes, but we limit our choice by ignoring those in which the shape could not correspond to the unit cell of a crystal.

- *Rotation Axis.* Clockwise rotation of $360^\circ/n$ about the axis. Crystals may have 2-fold (diad), 3-fold (triad), 4-fold (tetrad), or 6-fold (hexad) rotation axes; the 1-fold axis is always present. Any other rotation, such as a 5-fold axis, is not consistent with the requirement that a crystal lattice must have translational symmetry.
- *Mirror Plane.* When a plane can be chosen such that all features on one side of the plane appear, as if in a mirror, on the other side of the plane, then the crystal has a mirror plane (also known as a plane of symmetry). We call this an m plane.
- *Center of Symmetry.* If every feature in or on the object can be joined by an imaginary line through the center of the object to an identical feature, then we say the object has a center of symmetry.
- *Inversion Axis.* If when any point is rotated about an axis and then moved through the center of symmetry it arrives at an identical point, then the object has an inversion axis.

We refer to such axes as $\bar{1}$, $\bar{2}$, $\bar{3}$, $\bar{4}$, or $\bar{6}$ axes. Notice that the $\bar{1}$ axis is, in fact, describing a center of symmetry. The $\bar{2}$ axis is an alternative description of an m plane.

There are other symmetry elements such as screw axes that are meaningful for crystals but not for our macroscopic crystal shapes. Figure 5.3 illustrates some of the symmetry elements for a cube. The most important are the four 3-fold axes along the $\langle 111 \rangle$ diagonals.

TABLE 5.1 The Seven Crystal Systems

System	Relationship between lattice parameters	Example
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma \neq 90^\circ$	Turquoise Kyanite Albite feldspar
Monoclinic	$a \neq b \neq c$ $\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$	Monazite Titanite Orthoclase
Orthorhombic	$a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Olivine Brookite Stibnite
Tetragonal	$a = b \neq c$ $\alpha = \beta = \gamma = 90^\circ$	Zircon Rutile Hausmannite
Hexagonal	$a = b \neq c$ $\alpha = \beta = 90^\circ; \gamma = 120^\circ$	High quartz Wurtzite Beryl
Rhombohedral (or Trigonal)	$a = b = c$ $\alpha = \beta = \gamma \neq 90^\circ$	Ilmenite Calcite Corundum
Cubic	$a = b = c$ $\alpha = \beta = \gamma = 90^\circ$	Halite Magnetite Garnet

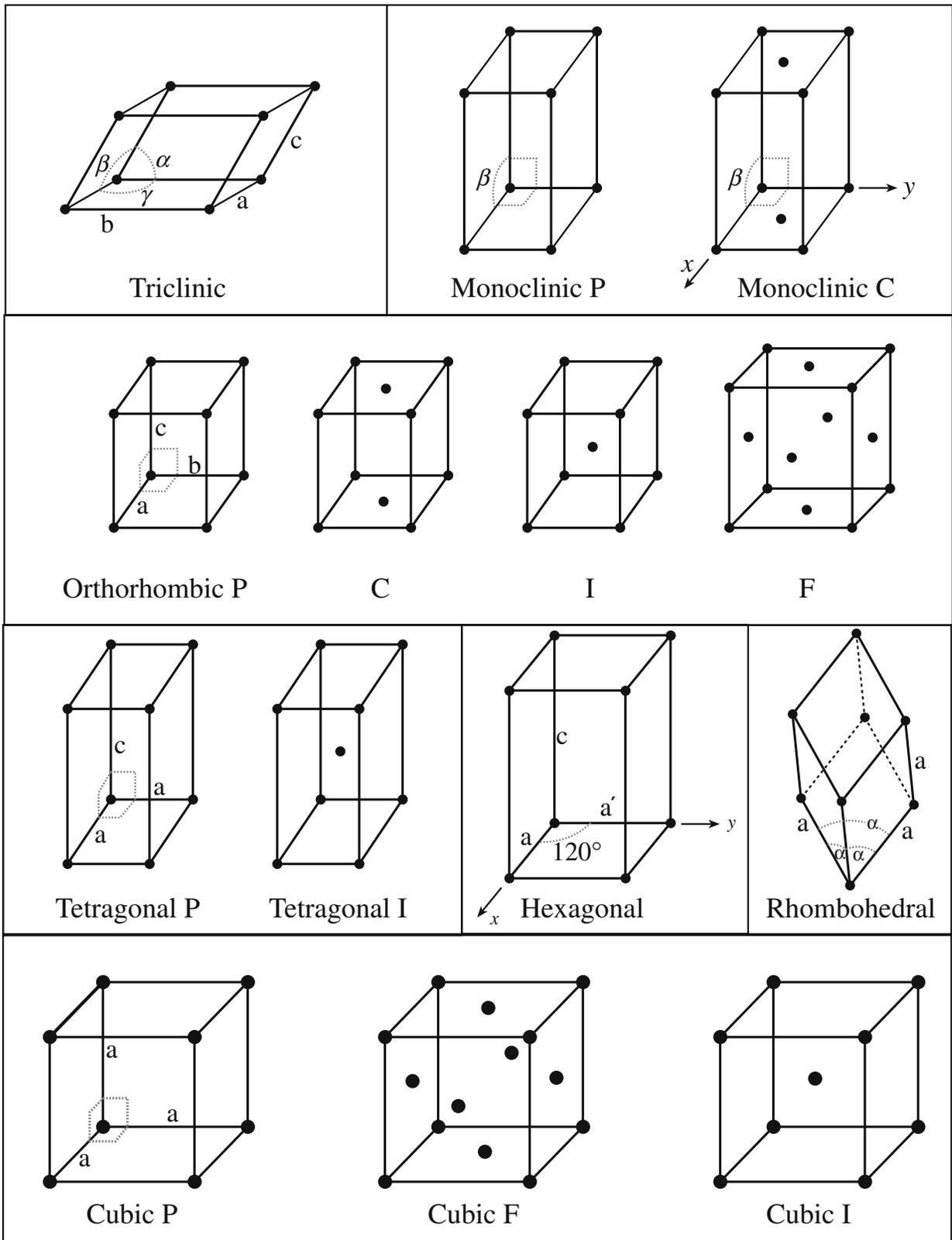
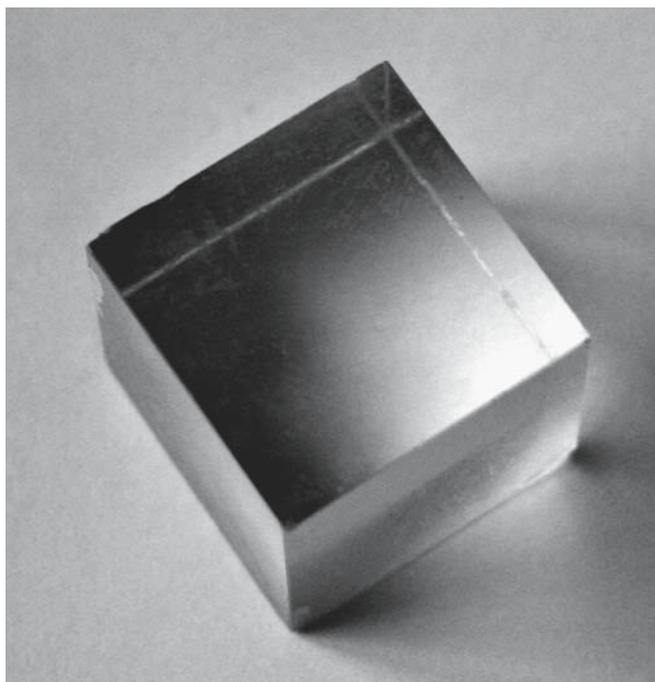


FIGURE 5.1 The fourteen Bravais lattices.



(A)



(B)

FIGURE 5.2 Crystals with faceted surfaces illustrating macroscopic symmetry elements; (a) MgO, (b) calcite.

5.2 SYMMETRY AND CRYSTALLOGRAPHY

Describing the symmetry of crystals is often more complicated than that of solid shapes such as the cube in Figure 5.3. For example, the crystal may have a cubic shape and belong to the cubic crystal system but not have the maximum internal symmetry.

Table 5.2 lists the Hermann–Mauguin notation for expressing the symmetry operators. Some combinations

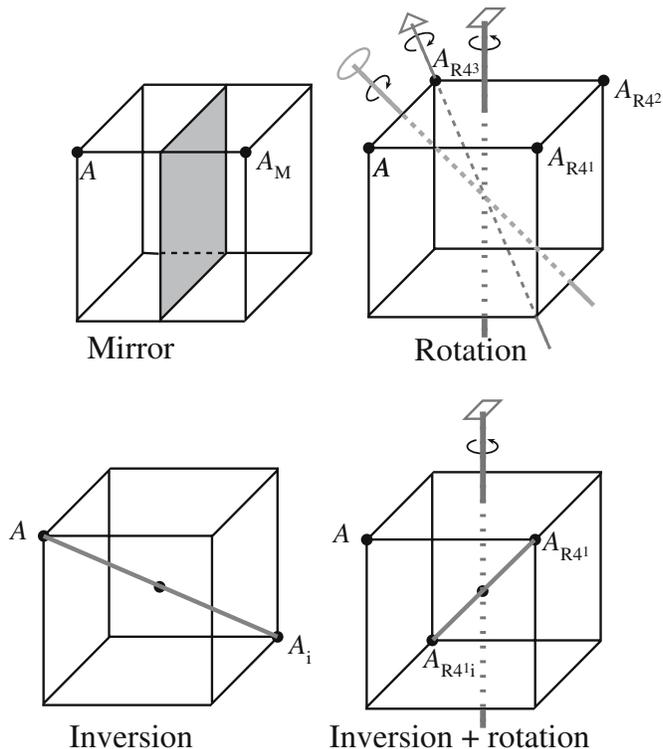


FIGURE 5.3 Symmetry elements for a simple cube.

of symmetry elements produce the same answer. For example, m is the same as $\bar{2}$ while $\bar{2}3$ and $2m3$ are both the same as $2/m3$, which is written as $m3$. So, as with any convention, the only way to get it right is to memorize it. Table 5.3 lists the symmetry operations associated with each of the seven crystal systems. The final column in Table 5.3 has the maximum possible symmetry and is called the holosymmetric point group. For example, NaCl is $m3m$ while FeS_2 is $m3$. Both crystals are cubic, but they have different symmetries; we will show the reasons for this in Chapter 6. The notation is not always the same as indicated at the top of the column. The symbols given here are known as the international convention. Actually we could write them out fully, but the reduced description contains the essentials; for example, $m3m$ is actually $\bar{4}/m3m$ and 43 is actually 432 .

TABLE 5.2 Symmetry Operators (Hermann–Mauguin Notation)^a

X	Rotation axis alone
\bar{X}	Inversion axis alone
X/m	Rotation axis with a symmetry plane <i>normal</i> to it
Xm	Rotation axis with a symmetry plane that is not normal to it (usually a vertical symmetry plane)
$\bar{X}m$	Inversion axis with a symmetry plane not normal to it
$X2$	Rotation axis with a diad normal to it
X/mn	Rotation axis with a symmetry plane normal to it and another not so

^aIn writing the symbol, the principal symmetry axis is placed first. For cubic, 3 is always second.

TABLE 5.3 The 7 Crystal Systems and the 32 Crystal Point Groups

Crystal system	Essential symmetry	X	\bar{X}	X/m	Xm	$\bar{X}m$	X2	X/mmm
Triclinic	1-fold axis	1	$\bar{1}$	—	—	—	—	—
Monoclinic	2-fold axis (parallel to y)	2	m	2/m	—	—	—	—
Orthorhombic	—	—	—	—	mm	—	222	mmm
Trigonal	3-fold axis (parallel to z)	3	$\bar{3}$	—	3m	$\bar{3}m$	32	—
Cubic	Four 3-fold axes	23	—	m3	—	$\bar{4}3m$	432	m3m
Tetragonal	4-fold axis (parallel to z)	4	$\bar{4}$	4/m	4mm	$\bar{4}32$	422	4/mmm
Hexagonal	6-fold axis (parallel to z)	6	$\bar{6}$	6/m	6mm	$\bar{6}m2$	622	6/mmm

You can find the full details of the international convention in the *International Tables for Crystallography* (1983). These symmetry operations or elements can be combined to provide 32 different crystal classes. The crystal classes are often called the crystal point groups. They are the point groups that are consistent with the translational symmetry of a crystal.

5.3 LATTICE POINTS, DIRECTIONS, AND PLANES

The notation used for identifying planes and faces of crystals is that of W.H. Miller and is referred to as the Miller indices of a plane. The lengths of the unit cell are *a*, *b*, and *c*. A family of planes cuts these axes at the origin and at $\frac{a}{h}$, $\frac{b}{k}$, $\frac{c}{l}$. The plane is then defined by the indices *h*, *k*, and *l*. If these indices are not all integers we multiply by the quotient to make them integers. Thus the intercepts $\frac{3}{2}a$, *4b*, and *1c* give *h*, *k*, and *l* values of $\frac{2}{3}$, $\frac{1}{4}$, and 1 and this *hkl* is 8.3.12. We use periods to separate the numbers only if one of them is greater than 9. If the intercept is negative we write \bar{h} (bar *h*, sometimes read as *h* bar).

Figure 5.4 illustrates some of the low-index planes in the orthorhombic crystal system. Since there may be different combinations of *hkl* that give symmetry-equivalent planes we use (*hkl*) to denote a particular plane and {*hkl*} to denote an equivalent set of planes. The faces of the cube form the set of {100} planes.

Directions are easier to define. The vector $U\mathbf{a} + V\mathbf{b} + W\mathbf{c}$ is simply written as [UVW]. We can then write <UVW> to denote all the equivalent directions formed by permuting *U*, *V* and *W*. The vector $U\mathbf{a} - V\mathbf{b} + W\mathbf{c}$ is denoted by

[$U\bar{V}W$]. Some low-index directions in the orthorhombic system are illustrated in Figure 5.5.

**CONVERTING NOTATION:
MILLER AND MILLER-BRAVAIS**

$$U = u - t \quad u = (2U - V)/3$$

$$V = v - t \quad v = (2V - U)/3$$

$$W = w \quad t = -(u + v) = -(U + V)/3$$

$$w = W$$

A special direction, known as the zone axis, is the one that is common to two planes $h_1k_1l_1$ and $h_2k_2l_2$. The directions [$h_1k_1l_1$] and [$h_2k_2l_2$] are the normals to the two planes and the zone axis [UVW] is then given by the vector cross-product. The zone axis has particular significance in electron

microscopy because it represents the direction of the incident electron beam with respect to the sample.

When discussing crystals with hexagonal symmetry, it is helpful to use Miller–Bravais indices because these clarify the symmetrically equivalent planes. In this scheme, a fourth index, *i*, is introduced such

MILLER INDICES

Low-index planes have small values of *h*, *k*, and *l* (and *i*). All are integers.

that $i = -(h + k)$. Figure 5.6 shows some planes and directions in the hexagonal system. The advantage of the four-index Miller–Bravais system, and the main reason for its use, is that similar planes have similar indices (as we saw in the case of the Miller system). For example, the planes (10 $\bar{1}$ 0), (01 $\bar{1}$ 0), ($\bar{1}$ 100), ($\bar{1}$ 010), (0 $\bar{1}$ 10), and (1 $\bar{1}$ 00) are the six sides (called prism planes) of the hexagonal lattice; these clearly are of similar type. In the Miller system, however, these will be (100), (010), ($\bar{1}$ 10), ($\bar{1}$ 00), (0 $\bar{1}$ 0), and (1 $\bar{1}$ 0), and they are definitely not of a similar type.

To transform directions, it is helpful to remember from Figure 5.6 that the vector [1 1 1 0] is a null vector: it has no length!

Thus we can change the three-index direction [1 1 0] in Figure 5.6 to its four-index form as follows [1 1 0] → [1 1 0 0] → [1+*f* 1+*f* *f* 0]. So that our four-index notation for directions is the same as for planes (i.e., $U + V + W = 0$), we want $2 + 3*f*$ to be zero. Thus $f = -\frac{2}{3}$ and the direction is [$\frac{1}{3} \frac{1}{3} -\frac{2}{3} 0$] or [1 $\bar{2}$ 0].

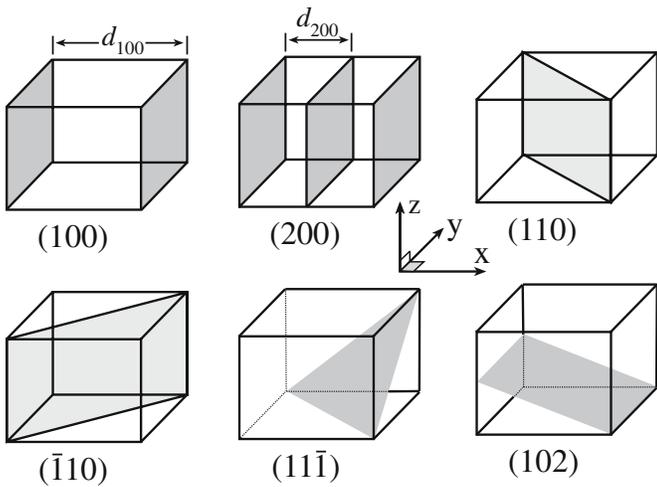


FIGURE 5.4 Miller indices of some lattice planes. The lattice-plane spacing is given by d_{hkl} .

The two notations are related and it is straightforward to convert between them. The Miller–Bravais system is widely used in ceramics because alumina (sapphire) often behaves as if it were hexagonal, although it is actually trigonal.

5.4 THE IMPORTANCE OF CRYSTALLOGRAPHY

Understanding the crystalline structure of ceramics is critical to understanding many of their properties.

- Diffusion. Often depends on the size and number of interstitial sites, both functions of the crystal structure.
- Deformation by slip or twinning. In ceramics there are both crystallographic and electrostatic considerations. The slip direction is usually along a close packed direction. The slip plane will usually be a closely packed plane or one that does not put like charges in

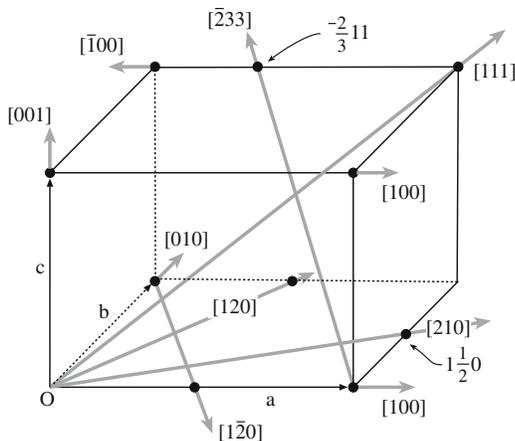


FIGURE 5.5 Indices of directions in an orthorhombic unit cell with examples of vectors included.

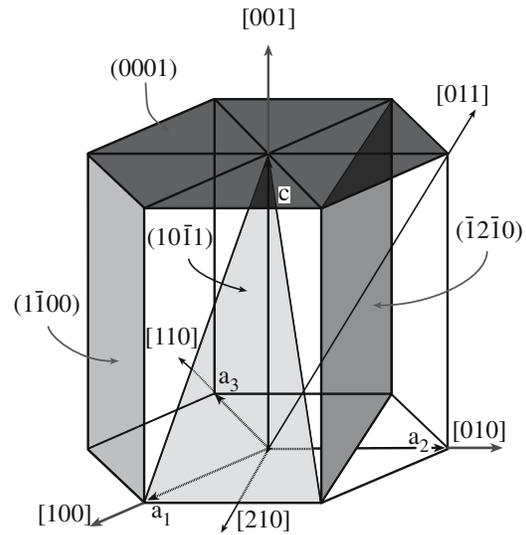


FIGURE 5.6 Indices of planes (using Miller–Bravais notation) and directions (using three-index Miller notation) in the hexagonal unit cell.

juxtaposition. Twin planes are usually special low-index planes.

- Piezoelectricity. Crystals must be noncentrosymmetric.
- Thermal conductivity. Phonon conductivity is most efficient in simple crystal structures formed by small atoms.
- Fracture. Often crystallographic, but not always (e.g., glass and cubic zirconia).
- Cleavage. Always crystallographic. Cleavage planes have high atomic density, but we also need to consider charge.
- Ferrimagnetism. In ferrimagnets the coordination number of the magnetic cation (usually an Fe ion) determines its behavior in an applied magnetic field.

To really appreciate the importance, and complexities, of the relationships between crystallography and properties, see Nye (1985).

5.5 PAULING'S RULES

Ceramic materials are often thought of as being ionically bonded and ions thought of as being charged spheres. Many important ceramics are oxides in which the oxygen anion is much larger than the cation. The crystal structure adopted by the material is based on a balance between the attractive and repulsive forces in the crystal. The electrostatic attractive force between ions of unlike charge implies that an ion with a high CN would be more stable than an ion with a low CN, that is, the electrostatic attraction is maximized. However, if too many ions of the same charge are clustered around an individual ion of the opposite charge, they begin to interfere with one another, that is, the electrostatic repulsion is maximized. There exists a

CN where the attraction is maximized and the repulsion is minimized. This number is determined by the ratio of the radii of the two ions. Questions then arise as to why certain oxides have the structure they do and how this affects mixing or doping of oxides.

Pauling proposed a set of rules to use when discussing such topics. These rules work so well that they are sometimes regarded as laws, which they are not. We will discuss the origin of the rules and then the rules themselves.

The idea is simply that ions of opposite sign pack together in such a way as to keep ions of like sign apart.

- Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii and the CN is determined by the radius ratio.
- Rule 2: In a stable structure, the total strength of the bonds that reach an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion.
- Rule 3: The polyhedra in a structure tend not to share edges or faces. If the edges are shared, the shared edges are shortened. Shared faces are the least favorable.
- Rule 4: Crystals containing different cations of high valence and small CN tend not to share polyhedron elements with each other.
- Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small.

When reading the discussion of these rules, keep in mind the following questions and remember that all rules have exceptions.

- Why do CsCl and NaCl have different structures?
- Why do Mg^{2+} ions tend to occupy tetrahedral sites while Al^{3+} ions occupy octahedral sites in spinel, when both ions occupy octahedral sites in MgO and Al_2O_3 ?
- Why do zinc blende and wurzite have different structures when both are ZnS? Why does GaAs have one structure and AlN have the other?
- What determines the structure of silicates? Are any other structures like this?
- Is the structure of $BaTiO_3$ important regarding its properties?

On Rule 1: A coordinated polyhedron of anions is formed about each cation. The cation–anion distance is determined by the sum of the two radii. CN is determined by the radius ratio:

A MNEMONIC

Ca^{2+} is a cation.

$$\text{Radius ratio} = \frac{r_M}{r_X} \quad (5.3)$$

A given CN is stable only when the ratio of cation to anion radius is greater than some critical value. These limits are given in Table 5.4. The derivation of these limits is strictly geometric as shown in Figure 5.7.

MX

M is the cation and is often a metal.
X is the anion and is never a metal.
You will sometimes see CA or +- instead of MX.

Why are the radius ratio and CN related? Coulomb interactions mean that like signs should be as far apart as possible and opposite signs as close together as possible.

Crystal structures are thus at their most stable when the cations have the maximum CN allowed by r_X . In many well-known ceramics, the cation coordination polyhedron is the basic building block.

On Rule 2: In a stable structure, the total electrostatic strength of the bonds, S , reaching an anion in a coordination polyhedron from all neighboring cations should be equal to the charge of the anion

$$S = \frac{Z_M}{\text{CN}} \quad (5.4)$$

where CN is the coordination number and Z_M = charge on the cation. The fundamental idea is that the crystal must be electrically neutral.

We can illustrate this idea for the oxygen anion. Each O^{2-} might bond to a combination of cations:

- Si^{4+} ions, $S = 4/4 = 1$. Two bonds of strength 1 reach the shared oxygen ion from the surrounding silicon ions. This is the case in, for example, cristobalite (a polymorph of SiO_2). The Si^{4+} are surrounded by four O^{2-} ions in a tetrahedral arrangement.
- Al^{3+} ions, $S = 3/6 = 1/2$. Each O^{2-} ion is surrounded by four Al^{3+} , each with a bond strength of 1/2. The Al^{3+} is surrounded by six O^{2-} ions in an octahedral arrangement. This is the case in, for example, corundum.
- In the mineral kyanite, Al_2SiO_5 , we have one Si^{4+} plus two Al^{3+} ions surrounding each O^{2-} ion. There are six O^{2-} around each octahedral Al^{3+} ion.
- In forsterite, Mg_2SiO_4 , we have one Si^{4+} ion plus three octahedral Mg^{2+} ions ($S = 2/6$). We need three Mg^{2+} ions to balance the charge.

Polyhedron	CN	Minimum (= r_M/r_X)
Cube	8	0.732
Octahedron	6	0.414
Tetrahedron	4	0.225
Triangle	3	0.155

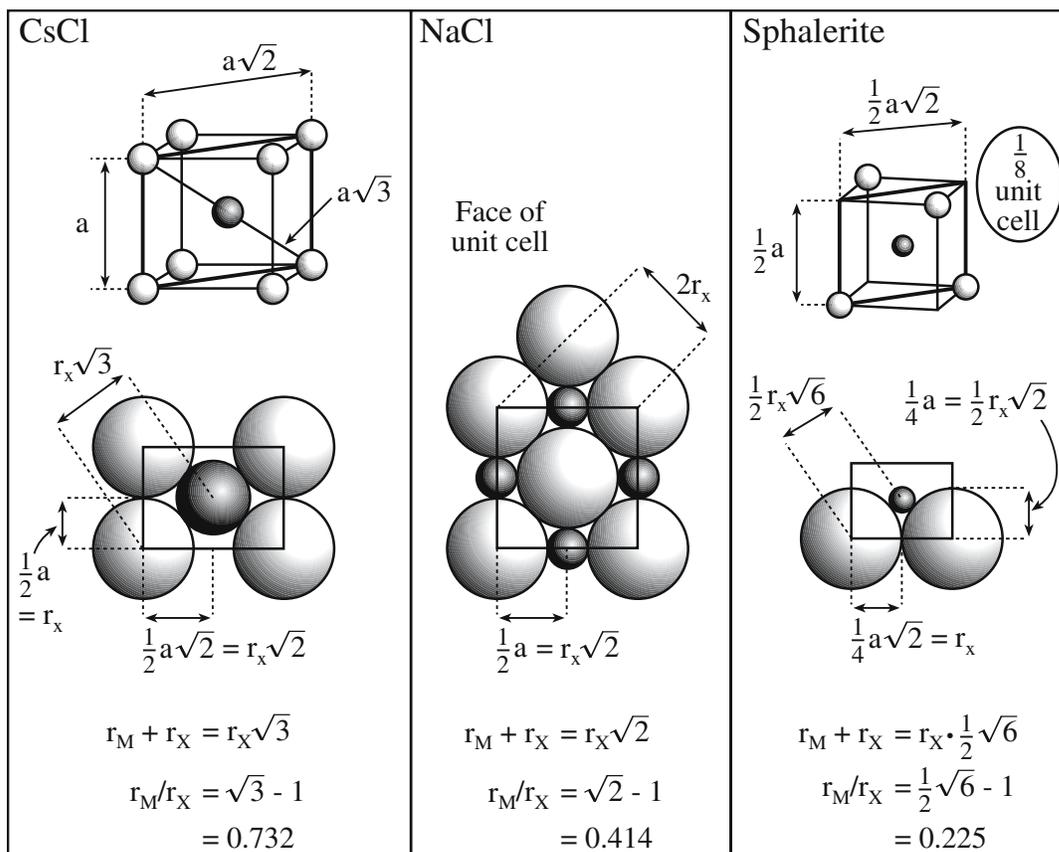


FIGURE 5.7 Geometric method for calculating limiting radius ratios.

In silicates, the Si atoms are each surrounded by four O^{2-} anions, so each O ion has an additional charge of -1 that must be used to bond to another ion. Thus, for an aluminosilicate, we need a large cation with a charge of $+1$ or $+2$ so it can be surrounded by eight or more oxygen ions. Calcium (with CN = 8) fits this requirement to give calcium aluminosilicate. Table 5.5 shows values of predicted CN and S for various cations.

On Rule 3: Polyhedra in a structure prefer not to share edges or faces. Clearly, if the faces are shared, then at least three edges are also shared.

This effect is large for cations with a high valence and small coordination number. In the first case, the charge on the cation is large increasing the Coulomb repulsion. It is especially large when the radius approaches the lower

limit of stability of the polyhedron. Thus, if two anion polyhedra have an edge or face in common, then the cations are being brought too close together. We can provide an alternative statement of the rule. The existence of edges, and particularly faces, common to two anion polyhedra in a coordinated structure decreases its stability.

Examples:

CsCl: the anions sit at the corners of cube and share faces.

NaCl: the anions sit at the corners of octahedra and share edges.

ZnS: The anions sit at the corners of tetrahedra and share vertices.

If polyhedra share edges, these edges tend to be shortened. We can think of this shortening as concentrating more “anion” between cations, which are too close together! The converse of the rule is that if you find an apparent violation it is likely that the bonding is not ionic. However, many materials with the ZnS structure, which does the best job of separating like ions, have predominantly covalent bonding. Determination of the fraction of ionic character in a bond can be made using Eq. 4.24.

Some examples:

TABLE 5.5 Predicted Coordination and Strength of the Bond

Ion	r_M/r_X	Predicted coordination	Strength of bond
Si^{4+}	0.29	4	1
Al^{3+}	0.39	4 or 6	$\frac{3}{4}$ or $\frac{1}{2}$ ($\frac{3}{4}$ or $\frac{3}{6}$)
Mg^{2+}	0.51	6	$\frac{1}{3}$ ($\frac{2}{6}$ $\frac{2}{6}$)
Ti^{4+}	0.44	6	$\frac{2}{3}$ ($\frac{4}{6}$)
K^{1+}	0.99	8	$\frac{1}{8}$

- In FeS₂ (iron pyrites, fool's gold and a ceramic) the [FeS₆] octahedra are linked by shared edges that are longer than expected.
- Silicates contain [SiO₄]⁴⁻ tetrahedra; in all cases, they share corners due only to strong mutual repulsion between Si⁴⁺. Again there is actually a large covalent component to the bonding.
- It is thus a geometric rule again, but is, nonetheless, important. For example, the edges of the occupied octahedra in Al₂O₃ are 0.25 nm long, not 0.28 nm long.

On Rule 4: Crystals containing different cations of high valence and small CN tend not to share polyhedron elements with each other. Sharing parts of polyhedra decreases the stability of the structure, so this rule is really a corollary to rule 3.

As an example, in CaTiO₃, [CaO₁₂] polyhedra share edges and [TiO₆] polyhedra share corners. The Ti⁴⁺ cation is more highly charged than the Ca²⁺ cation, so the CN is smaller; the Coulombic repulsion between cations is proportional to the product of the charges.

On Rule 5: The number of essentially different kinds of constituents in a crystal tends to be small. As far as possible, the environment of chemically similar atoms will be similar (and Pauling's analysis assumes that the bonding is all ionic).

If all types of bonding are possible, it is difficult to predict what will happen, but if every oxygen has the same environment then there is only one possibility. The result is actually found in garnet. This rule only requires the ions to be SIMILARLY COORDINATED. Their actual geometric positions need *not* be equivalent. They are *not* structurally indistinguishable. The rule actually has limited value because in a majority of silicates, the oxygen ions do not have like environments.

5.6 CLOSE-PACKED ARRANGEMENTS: INTERSTITIAL SITES

A close-packed structure is one that has the maximum volume of the unit cell occupied by atoms. The occupied fraction of the unit cell can be determined by calculating the atomic packing factor (APF):

$$\text{APF} = \frac{\text{number of atoms per cell} \times \text{volume of one atom}}{\text{volume of unit cell}} \quad (5.5)$$

The *maximum* possible APF for packing of spheres all having the same size is 0.74. This arrangement is the one

seen in grocery stores in which oranges in adjacent layers sit off-center, resting within the pocket created by the oranges sitting side by side below. Materials scientists and crystallographers (as well as greengrocers) have known that this is the most efficient way to stack a bunch of round objects, but mathematicians took a long time to be convinced (see the interesting book on this topic and other mathematical riddles by Singh, 1997). A mathematical proof for what is known as the Kepler conjecture was announced in 1998 and the manuscript was published 7 years later (Hales, 2005).

Crystal structures having an APF of 0.74 are called close-packed structures. There are only two close-packed structures:

- Face-centered cubic (fcc)
- Hexagonal close-packed (hcp)

We will consider the fcc and hcp structures in some detail because they are so common. For the fcc structure all the points are actually lattice points. In the hcp structure this is not the case. Thus we should never say the "hcp lattice" but we do. The hcp structure describes a particular arrangement of similar atoms, but it is not a lattice of identical points.

The relationship between the fcc and hcp structures is illustrated in Figure 5.8a. The atoms on the (111) planes of the fcc structure are arranged in a hexagonal pattern just like the atoms on the (0002) planes of the hcp structure. The only difference between the two structures is the way in which these hexagonal sheets of atoms are arranged above one another. In the hcp structure, the atoms in the second layer are above the hollows in the first layer and the atoms in the third layer are above the atoms in the first layer, so the stacking sequence can be summarized as A B A B A B . . . The stacking in the hcp structure is illustrated in Figure 5.8b. The first two atom layers in the fcc structure are put down in the same way, but the atoms of the third layer are placed in the hollows of the second layer; not until the fourth layer does a position repeat. The stacking sequence for fcc is therefore A B C A B C A . . . This sequence is illustrated in Figure 5.8c.

In predominantly ionically bonded oxide ceramics, the O²⁻ ion approximates a sphere. So we can view these structures as based on a close-packed arrangement of spheres and then filling the remaining space. We must remember that the anions are not necessarily touching, but they are merely arranged in a way that is the same as that in the close-packed structures.

GARNET			
Ca ₃ Al ₂ Si ₃ O ₁₂ is not only a gemstone but also a ceramic. Other garnets such as yttrium aluminum garnet (YAG) and gallium gadolinium garnet (GGG) are technologically much more important materials.			
Ion:	Ca ²⁺	Al ³⁺	Si ⁴⁺
O ²⁻ coordination	8	6	4
O bond strength, <i>S</i>	$\frac{2}{8} = \frac{1}{4}$	$\frac{3}{6} = \frac{1}{2}$	$\frac{4}{4} = 1$

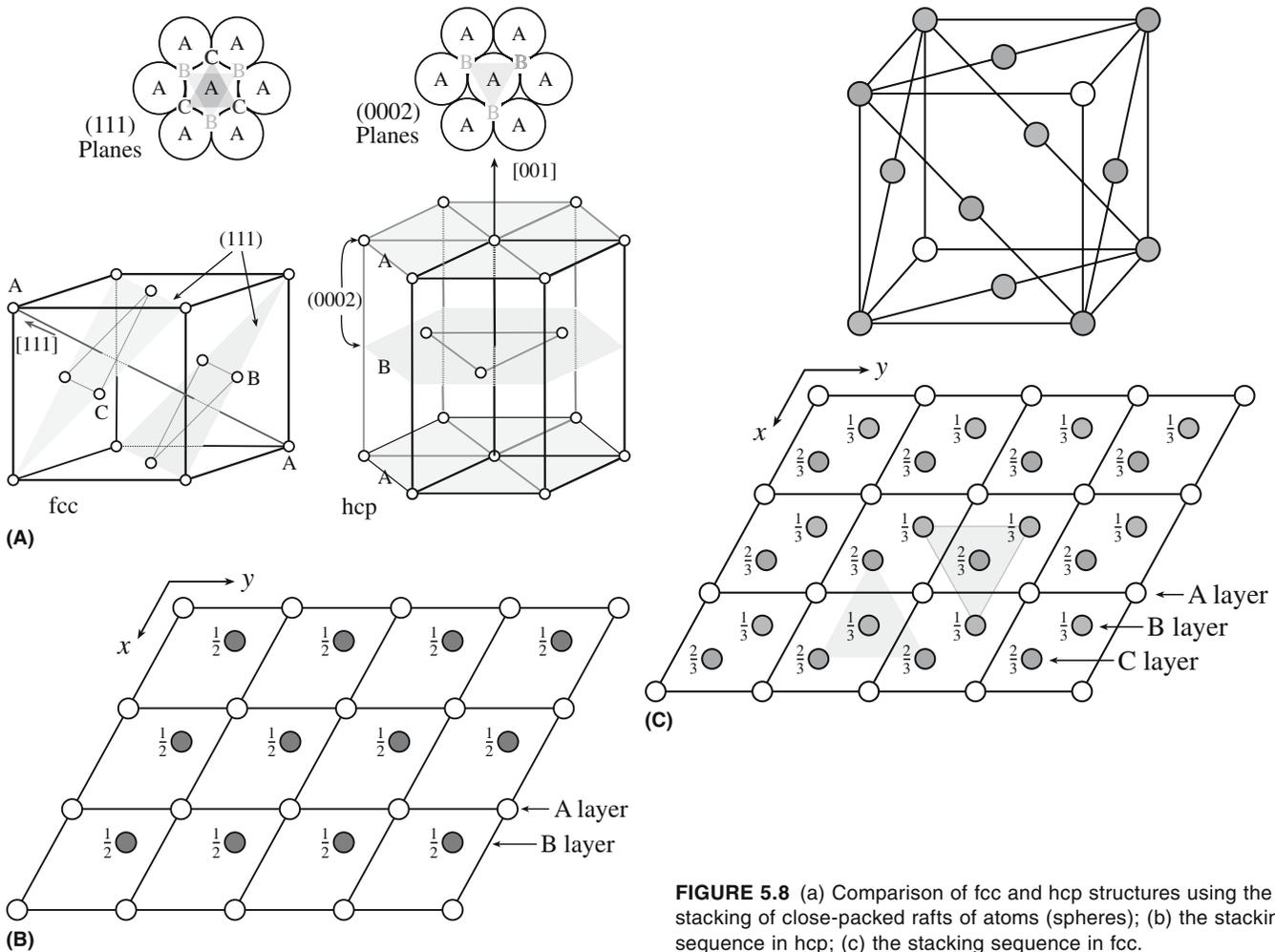


FIGURE 5.8 (a) Comparison of fcc and hcp structures using the stacking of close-packed rafts of atoms (spheres); (b) the stacking sequence in hcp; (c) the stacking sequence in fcc.

So we now need to answer the following questions:

- Where are the interstitial sites?
- What is their CN?
- How many sites are there?

The fcc and hcp arrangements offer both octahedral and tetrahedral interstices, making them good hosts for cations, since two size ranges can be incorporated. Both fcc and hcp arrangements can be stabilized by filling just the tet-

rahedral sites or just the octahedral sites. The fcc lattice can be stabilized by filling a combination of tetrahedral and octahedral sites. In the fcc arrangement there are eight tetrahedral sites and four octahedral sites per cell. The location of these sites is shown in Figure 5.9a. There are four tetrahedral sites and two octahedral sites per cell in the hcp arrangement. The location of these sites is shown in Figure 5.9b.

In ceramics the APF is always < 0.74 , even though we have increased the number of atoms per cell. As an

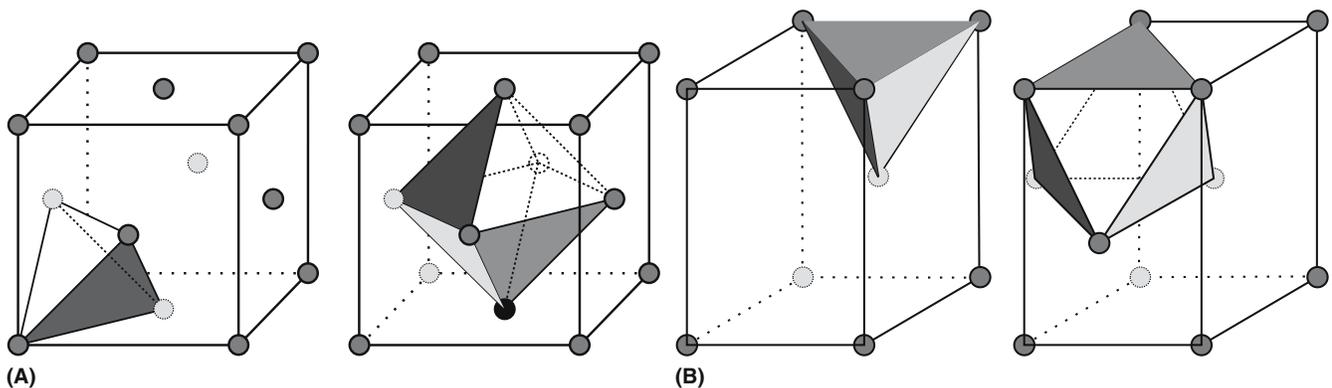


FIGURE 5.9 (a) Interstitial sites in the fcc structure; (b) interstitial sites in the hcp structure.

TABLE 5.6 The Strukturbericht Notation

Symbol	Definition	Symbol	Definition
A	Element	E-K	Complex
B	AB compounds	L	Alloys
C	AB ₂	O	Organic
D	A _m B _n	S	Silicates

example, if we fill all the octahedral sites in an fcc arrangement of O²⁻ with cations (e.g., Mg²⁺) as we'll see in Chapter 6, the APF is 0.69. In other words, 69% of the cell volume is occupied by ions.

5.7 NOTATION FOR CRYSTAL STRUCTURES

One of the things you will notice is that many crystal structures are named after particular materials (often a naturally occurring mineral) that exhibit the structure. There are no systematic names for crystal structures, as there are, for example, for organic compounds, which are named using a system recommended by the International Union of Pure and Applied Chemistry (IUPAC). This system provides us with a systematic way of naming many organic compounds on sight and the name indicates the structure of the compound. A similar system is not used for naming crystal structures. However, there are several different notations for specifying crystal structures that can be very useful.

- *Strukturbericht*. The symbol consists of a letter that characterizes the type of structure and a number designating a specific type within a letter category. The rules are given in Table 5.6.
- *Pearson*. The symbols give, successively, the crystal system, the Bravais lattice symbol, and the number of atoms per unit cell. The notation is summarized in

TABLE 5.7 Symbols Used in The Pearson Notation

Symbol	System	Lattice
aP	Triclinic (anorthic)	P
mP	Simple monoclinic	P
mC	Base-centered monoclinic	C
oP	Simple orthorhombic	P
oC	Base-centered orthorhombic	C
oF	Face-centered orthorhombic	F
oI	Body-centered orthorhombic	I
tP	Simple tetragonal	P
tI	Body-centered tetragonal	I
hP	Hexagonal	P
hR	Rhombohedral	R
cP	Simple cubic	P
cF	Face-centered cubic	F
cI	Body-centered cubic	I

TABLE 5.8 Notation for Different Crystal Structures

Strukturbericht	Prototype	Pearson	Space group
A1	Cu	cF4	Fm $\bar{3}$ m
A2	W	cI2	Im $\bar{3}$ m
A3	Mg	hP2	P6 ₃ /mmc
A9	Graphite	hP4	P6 ₃ /mmc
B _h	WC	hP2	P6m2
B _k	BN	hP4	P6 ₃ /mmc
B1	NaCl	cF8	Fm $\bar{3}$ m
B2	CsCl	cP2	Pm $\bar{3}$ m
B3	Sphalerite	cF8	F4 $\bar{3}$ m
B4	Wurtzite	hP4	P6 ₃ mc
B10	PbO	tP4	P4/nmm
B26	CuO	mC8	C2/c
C2	FeS ₂ (pyrite)	cP12	Pa $\bar{3}$
C3	Ag ₂ O	cP6	Pn $\bar{3}$ m
C4	TiO ₂ (rutile)	tP6	P4 ₂ /mnm
C6	CdI ₂	hP3	P $\bar{3}$ ml
C7	MoS ₂	hP6	P6 ₃ /mmc
C8	High quartz	hP9	P6 ₂ 22
C9	β Cristobalite	cF24	Fd $\bar{3}$ m
C10	β Tridymite	hP12	P6 ₃ /mmc
C18	FeS ₂ (marcasite)	oP6	Pnnm
C21	TiO ₂ (brookite)	oP24	Pbca
C43	ZrO ₂	mP12	P2 ₁ /c
D0 ₉	ReO ₃	cP4	Pm $\bar{3}$ m
D0 ₁₁	Fe ₃ C	oP16	Pnma
D5 ₁	α -Al ₂ O ₃	hR10	R $\bar{3}$ c
D5 ₂	La ₂ O ₃	hP5	P $\bar{3}$ c1
D5 ₃	Mn ₂ O ₃	cI80	Ia $\bar{3}$
E2 ₁	CaTiO ₃	cP5	Pm $\bar{3}$ m
H1 ₁	MgAl ₂ O ₄	cF56	Fd $\bar{3}$ m
L1 ₀	AuCu	tP2	P4/mmm
L1 ₁	CuPt	hR32	R $\bar{3}$ m
L1 ₂	AuCu ₃	cP4	Pm $\bar{3}$ m

Table 5.7. Even though you will be able to find out the crystal system, the Bravais lattice, and the number of atoms from this notation, you will not be able to differentiate among different structures with similar notations. For example, cF8 refers to sodium chloride, diamond cubic, and zinc blende structures, which are different from one another.

Examples of Strukturbericht and Pearson symbols are given in Table 5.8.

5.8 STRUCTURE, COMPOSITION, AND TEMPERATURE

Many ceramics exist in different structures at different temperatures. These structures are known as polymorphs and we will give some examples in Chapter 6. The most stable structure at any particular temperature is governed by its free energy, *G*. The polymorph with the lowest free energy is the most stable. Expressions for the free energy and internal energy were given in Chapter 3. Both the internal energy, *E*, and the entropy, *S*, depend on crystal structure.

The following rules can be given for the temperature and pressure dependence of thermodynamically stable structures:

- At $T = 0$, $G = E$, that is, the free energy is fixed by the internal energy.
- At $T > 0$, the TS term becomes increasingly important and structures with a low degree of order are favored.
- At a sufficiently high temperature a polymorph with a larger S may achieve a lower G in spite of its larger E , as illustrated in Figure 5.10. The increased values of E and S of the high-temperature forms correspond to more open structures (larger specific volumes) with higher symmetry.
- There are two components to entropy (both increase as T increases)—thermal entropy and configurational entropy.
- In the liquid state, the order is even lower and it is the lowest in the gaseous state. Raising the temperature will lead to melting and finally to evaporation.
- Higher pressures favor structures that occupy a lower volume, that is, that have a higher density.

The crystal structure of a ceramic also depends on composition. As an example, consider three oxides of iron:

1. Wüstite (FeO): Cubic rocksalt structure. Iron is in the 2+ oxidation state.
2. Hematite (Fe_2O_3): Rhombohedral corundum structure. Iron is in the 3+ oxidation state.
3. Magnetite (Fe_3O_4): Cubic spinel structure. Iron is in 3+ and 2+ oxidation states.

The reasons for these differences are explained by Pauling's rules.

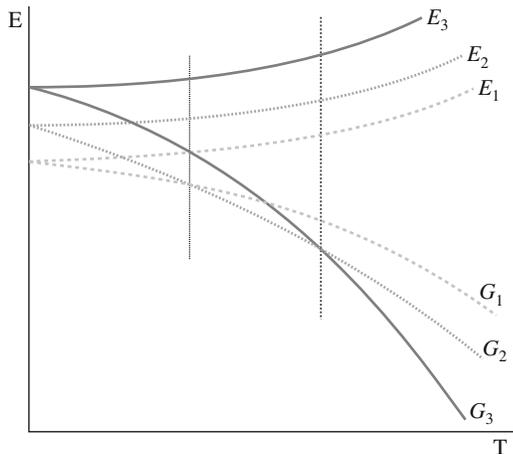


FIGURE 5.10 Schematic showing the relationship between internal energy E and free energy G of three polymorphic forms: $E_3 > E_2 > E_1$ and $S_3 > S_2 > S_1$. The form with the lowest G will be the one usually found at a specific temperature.

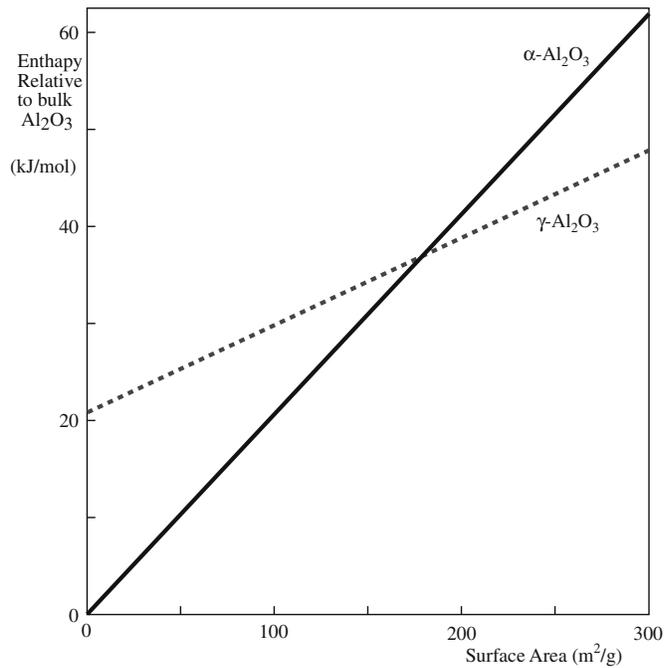


FIGURE 5.11 Calculated enthalpy of alumina (γ - and α -) polymorphs as it varies with the surface area. The calculation is an MD simulation using data for small surface areas. A large surface area per gm implies small particles.

There is another factor that can influence the equilibrium structure of a material and that is surface energy. The effect of surface energy has become of increasing importance with the interest in nano-sized particles of ceramics. When particle size becomes very small the fraction of atoms on the surface becomes very large. Surface energy effects can then dominate as illustrated in Figure 5.11, which shows that $\gamma\text{-Al}_2\text{O}_3$, rather than $\alpha\text{-Al}_2\text{O}_3$, can become the thermodynamically stable phase of aluminum oxide when the surface area exceeds $\sim 175 \text{ m}^2/\text{g}$. The key thing to remember is that nanomaterials do not always behave the same as the bulk material.

5.9 CRYSTALS, GLASS, SOLIDS, AND LIQUID

Classically, there are three distinct states of matter: gas, liquid, and solid. (The newer two, plasma and Bose-Einstein condensates, are not applicable to our discussion so we omit them.) In the previous section we noted how as temperature increases it is thermodynamically favorable for transitions to occur from a more ordered form to a less ordered one. The atoms or molecules that make up a gas are randomly arranged (E and S are high) and widely separated. A gas will fill all the available space inside a container. The atoms or molecules that make up a liquid are also randomly arranged, but they are closer together than those in a gas and they move relative to one another. The characteristic of a liquid is that it will fill a container

to the extent of its own volume. The third state of matter is solid, which can be defined as having a fixed shape. Solids can be classified as either *crystalline* or *noncrystalline*.

When we discuss crystals we are concerned with interatomic bonding, interatomic distances, the environment of the ions and long-range ordering. All of these concepts, except for long-range ordering, are relevant to noncrystalline materials such as glass. In fact, when we discuss silica-based glasses, the main point is how we do or do not link SiO₄ tetrahedra together. The concept of order that is important is separating the different classes of condensed matter. The basic differences are summarized below:

Crystal	Ordering on lattice—long-range order
Glass	Short-range order
Liquid	No order to short-range order

There are many amorphous ceramics (glasses). There are fewer amorphous semiconductors and some amorphous metal alloys. The main consideration, as you will see in Chapter 21, is the rate of cooling necessary to avoid crystallization. In many oxides the critical rate of cooling is very easy to achieve because the number of components is large and we have directional (covalent) bonding. The latter consideration also holds for the semiconductors, but for metal alloys we usually can rely only on frustrating crystallization using complex compositions and rapid quenching.

5.10 DEFECTS

One reason that we need to understand the structure of perfect crystals is so that we can begin to understand imperfect crystals. The topic is not just specific to ceramics. The interaction of defects is often most important to us. For ceramics, a special example of such interactions occurs in grain growth. Grain-boundary movement in ceramics usually involves the movement of point defects.

Understanding atomic bonding helps us understand the structures of crystals and glass. When we think of crystals, we think of atoms arranged in a perfect way. We traditionally think in terms of crystal defects, but we will also consider how these ideas apply to defects in glass.

One question to keep in mind is “how is this feature different from metals?” The answer is not always as obvious as it might seem at first, because we often compare ceramic materials to particularly simple (usually fcc) metals. Apart from carbon and the elemental semiconductors, Si and Ge, all ceramics contain two or more different atoms, so we should at least compare them with metal alloys not pure metals. The next question is “how do defects influence the properties of the ceramic?” For that we need to understand defects first.

We classify defects as having 0, 1, 2, or 3 dimensions, as shown in Table 5.9. Actually all of the defects we will

TABLE 5.9 Hierarchy of Crystal Lattice Defects

“Dimension”	Defect	Some topics
0	Point defects	Geometry, strain energy, charge
1	Line defects	Geometry, energy
2	Surfaces Grain boundaries Phase boundaries	Thermodynamics Structure, chemistry, wetting Phase distribution
3	Volume defects	Precipitates, particles, and voids

discuss are three-dimensional defects. Ceramics usually have mixed bonding, that is, a combination of ionic and covalent bonding. So, when we introduce defects, we usually change the local distribution of charge or break bonds, depending on which type of bond predominates. Any change in charge distribution can produce long-range effects. A broken covalent bond is known as a dangling (unpaired electron) bond that also behaves like a localized charge.

We have discussed the packing of ions in terms of coordination polyhedra. When we create defects in a crystal we can create new polyhedra that are not found in the perfect crystal. Pauling’s rules were developed for perfect crystals, but the principles still apply when we examine defects. One complication is that as we introduce grain boundaries, for example, new sites are produced that depend on the detailed nature of the grain boundary. Amorphous materials present a new challenge when describing point defects. Two amorphous materials can have different structures that depend on the processing history even if the chemistry is the same.

5.11 COMPUTER MODELING

Computer modeling of oxide structures and of defects in oxides is becoming more important, in part because the code is improving, but mainly because faster computers can make more realistic calculations. The problems for ceramic materials are those discussed in Chapters 3 and 4. If the bonding is ionic, then the ion–ion interactions are both strong and long-range. If there is a covalent component to the bonding, then the bonds have a directional character. (Glasses exist in a metastable state so their structure is, by definition, not the equilibrium one.) The problem is 2-fold. We need a computer code that can handle the long-range interactions. Even simple ceramics can have large unit cells, which means that the computer must be able to handle a large number of atoms.

We will summarize the approaches being used by different researchers to calculate properties of ceramics. This discussion is very brief and incomplete, but it should provide an idea of how the subject is developing. One

encouraging feature is that software packages that are suitable for the knowledgeable researcher who is not an expert programmer are becoming available commercially. These packages fall into two categories that can be linked. In one the atomic structure of a ceramic crystal can be displayed after inputting the appropriate crystal parameters. Such programs are simply using the rules of crystallography to generate the structures. The other, and far more complex, programs also use the interatomic potentials to deduce features of the structure and are performed using molecular dynamic (MD) approaches.

Terms Used in Modeling

We will begin by listing some of the terms you will encounter: *Pseudo-potential* is an expression that is being used to represent a real crystal potential. An equation like Eq. 4.1 is chosen and the parameters changed until a calculated value is obtained that agrees well with the known value of a physical parameter. This process will be carried out simultaneously for several parameters that are chosen to have some relevance to what you would like to calculate. *Electronic structure calculation*: Although ceramics are thought of as insulators, the electrons are important in understanding optical properties, for example.

Computer Modeling of Structures: The Need for Potentials

Most ceramics cannot be modeled from first principles simply because we do not know the potentials well enough. So the challenge with modeling crystals is that we have to use a model for the potential. These are available for Si and are quite good for Al_2O_3 and MgO .

We can summarize the problems for modeling ceramics as follows:

- Ceramics usually contain charged species. This means that the interionic forces extend over very large distances (remember the Madelung constant). To model such materials we need large unit cells. This problem becomes more difficult when we model defects.
- When the ceramic is covalent or has a large covalent component to the bonding, directions are important. Si is the classic example of a covalent material and can be modeled, but only because enormous effort could be justified by its commercial importance. Modeling silicates, which also have a large covalent component, is less developed.

Ceramics lag behind metals for two reasons. First, most ceramics contain more than one component so we need to have potentials for each ion. (FeO contains three ions for this purpose.) Second, the potentials have to be used to predict known quantities and these are not usually as well known as they are for metals.

A number of software packages are now available as shareware or commercially. One such program is GULP: the acronym stands for Generalized Utility Lattice Program. GULP can be used to perform different types of simulation on three-dimensional periodic solids and on isolated defects in such materials. GULP simulates structures of ionically bonded materials using a shell model and uses the crystal symmetry to accelerate the calculations and to simplify the input. These two factors can make it faster and more efficient than other programs. If you use GULP, for example, you will have access to at least 23 different potentials or models, including Buckingham, Morse, Coulomb, and Stilingger-Weber. Examples of the uses of GULP are modeling Al_2O_3 , defects in garnets, zeolites, and molecular sieves, and the structure of Al_2SiO_5 polymorphs. CeriusTM, another software package for simulating structures, also includes diffraction modules.

CHAPTER SUMMARY

This is the chapter in which we introduce crystallography. Some students object to having to learn this material. Our view is that you cannot understand point defects, piezoelectricity, grain boundaries, elasticity of noncubic crystalline materials, etc., unless you understand the differences between the different crystal structures, and for this you must understand the principles of crystallography. Pauling's rules for ionic ceramics give us a set of tools to allow us to predict the coordination of ions and even to guess the structure of a crystal that may be new to us. The exceptions to these rules often result from the presence of a covalent component to the bonding, which itself gives clues to the coordination. Once we know the crystal structure, we can predict what point defects might occur and even guess at the energies involved—just from counting broken bonds, for example. The best-known examples of such point defect sites are the octohedra and tetrahedral in the close packed (fcc or hcp) lattices, but we find these polyhedra in many different crystal structures, though they may be more difficult to recognize elsewhere. So just by considering Pauling's rules, we are introduced to one of the most useful concepts of solid-state chemistry—the concept of crystals being constructed by arranging polyhedra. The polyhedra are clusters of atoms that behave in quite systematic ways. As we will see in the following chapters, the most important of these polyhedra will be the tetrahedron formed by four oxygen ions with an Si ion at the center, but it is certainly not the only polyhedron of interest to us.

PEOPLE IN HISTORY

- Bravais, Auguste (1811–1863) presented his ideas on crystallography to the French Academy of Sciences in 1849. He was interested in a number of fields including botany, astronomy, and physics. It is for his work in crystallography that he is best remembered.
- Goldschmidt, Victor Moritz was born in Zurich, but spent his scientific career in Norway (1888–1947). Like Pauling, he derived rules for ionic radii.
- Haiüy, René-Just (1743–1822) published his essay in 1784 on a theory of the structure of crystals; the story is that his interest in crystals began when he examined a specimen of calcite that he had accidentally just dropped.
- Hooke, Robert (1635–1703) published *Micrographica* in 1665 showing images taken with his microscope. A genius.
- Miller, William Hallows (1801–1880) was born in South Wales and was Professor of Mineralogy at Cambridge University from 1832 until he died. He wrote the book that explained the notation developed by William Whewell (who also coined the word scientist); he gave full credit to the pioneering work of his mentor, Whewell, but we still refer to Miller indices.
- Wulff, Georgii (Yurii) Viktorovich was a Russian crystallographer born in 1863. The initial G was used in translations of his papers rather than the Y. He died in 1925 in Moscow.
- Wyckoff, Ralph Walter Graystone was born in 1897 and died in 1994. He was the author of the classic book, *The Stucutre of Crystals*, 1931.

GENERAL REFERENCES

- A great source for further reading lies in the mineralogical literature. The books by Putnis (1992), Deer, Howie, and Zussman (1992), etc. provide great insight, as does the literature from solid-state chemistry such as the books of Wells (1970), Hyde and Anderson (1989), etc. These references are given in Chapters 6 and 7.
- Barrett, C.S. and Massalski, T.B. (1980) *Structure of Metals*, 3rd edition, Pergamon, New York. Together with Pearson (below) gives more on the Strukturbericht notation.
- Buerger, M. (1978) *Elementary Crystallography*, The MIT Press, Cambridge, MA. One of the best introductions to the subject. At the level of this text.
- Burdett, J.K. (1995) *Chemical Bonding in Solids*, Oxford University Press, Oxford.
- Crystal modeling on a Macintosh or using Windows XP is easy using CrystalMaker. <http://www.crystalmaker.co.uk>.
- Gale, J.D. (1996) Empirical potential derivation for ionic materials, *Phil. Mag. B*, **73**, 3.
- Giacovazzo, C. *et al.* *Fundamentals of Crystallography*, 2nd edition, IUCr/Oxford University Press, Oxford. Comprehensive.
- International Tables for Crystallography*, Vol. A, 5th edition (2002), edited by T. Hahn, D. Reidel, Boston.
- Molecular Simulations Inc. (MSI) produces CeriusTM. The corresponding structure modeling package is CASTEP. <http://www.msi.com/materials/cerius2/castep.html#info>.
- Nyberg, M., Nygren, M.A., Pettersson, L.G.M., Gay, D.H., and Rohl, A.L. (1996) “Hydrogen dissociation on reconstructed ZnO surfaces,” *J. Phys. Chem.* **100**, 9054.
- Phillips, F.C. (1972) *An Introduction to Crystallography*, 4th edition, Wiley, New York. Includes a clear description of the Herman–Mauguin notation and the 32 classes of crystal symmetry. First published in 1946.

SPECIFIC REFERENCES

- Gale, J.D. (1997) “GULP—a computer program for the symmetry adapted simulation of solids,” *JCS Faraday Trans.* **93**, 629.
- Hales, T.C. (2005) “A proof of the Kepler conjecture,” *Ann. Math.* **162**, 1065. The paper is 121 pages long! Twelve reviewers spent more than 4 years reviewing it.
- Nye, J.F. (1985) *Physical Properties of Crystals*, Clarendon Press, Oxford.
- Pearson, W.B. (1972) *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley, New York. Gives many more details on crystal notation (see also Villars and Calvert below).
- Singh, S. (1997) *Fermat’s Last Theorem*, Fourth Estate, London.
- Villars, P. and Calvert, L.D. (1985) *Pearson’s Handbook of Crystallographic Data for Intermetallic Phases*, Vols. 1, 2, 3, ASM International, Metals Park, OH.

EXERCISES

- 5.1 Calculate the percentage of free space in an fcc stacking of spheres and a cubic stacking of spheres. Relate the result to two important different ceramic structures.
- 5.2 Based on Pauling’s radii, how do you expect the lattice parameters of Si and SiO₂ (high cristobalite) to compare? How does this fit with experiment? Discuss.

- 5.3 When the {111} planes of SiC stack with the sequence ABABAB, the SiC has hexagonal symmetry. When they stack with the sequence ABCABC, it has cubic symmetry. What symmetry does it have when it stacks ABCBABCBAABCBA? Explain your reasoning.
- 5.4 The face-centered cubic cell may be referred to the rhombohedral cell. Using a sketch show the relationship between the two cells.
- 5.5 Are there any interstices in hcp that are not present in fcc?
- 5.6 Why is there no Bravais lattice called orthorhombic A, monoclinic B, or tetragonal C?
- 5.7 If a sapphire crystal showed only one type of rhombohedral plane and the two basal planes, what would the shape of the crystal be?
- 5.8 FeS is a more complicated structure than FeO. Why would you not be surprised at this result?
- 5.9 In calcite (CaCO_3) the Ca^{2+} ion has a CN 6. Using the appropriate Pauling rule determine the ion environment around each O^{2-} ion.
- 5.10 From the ionic radii given, estimate the coordination numbers for the following oxides: (a) MgO, (b) Al_2O_3 , (c) Li_2O ; Li^+ 76 pm; O^{2-} 140 pm; Mg^{2+} 72 pm; Al^{3+} 54 pm.