4.8

The Structure and Properties of Solids

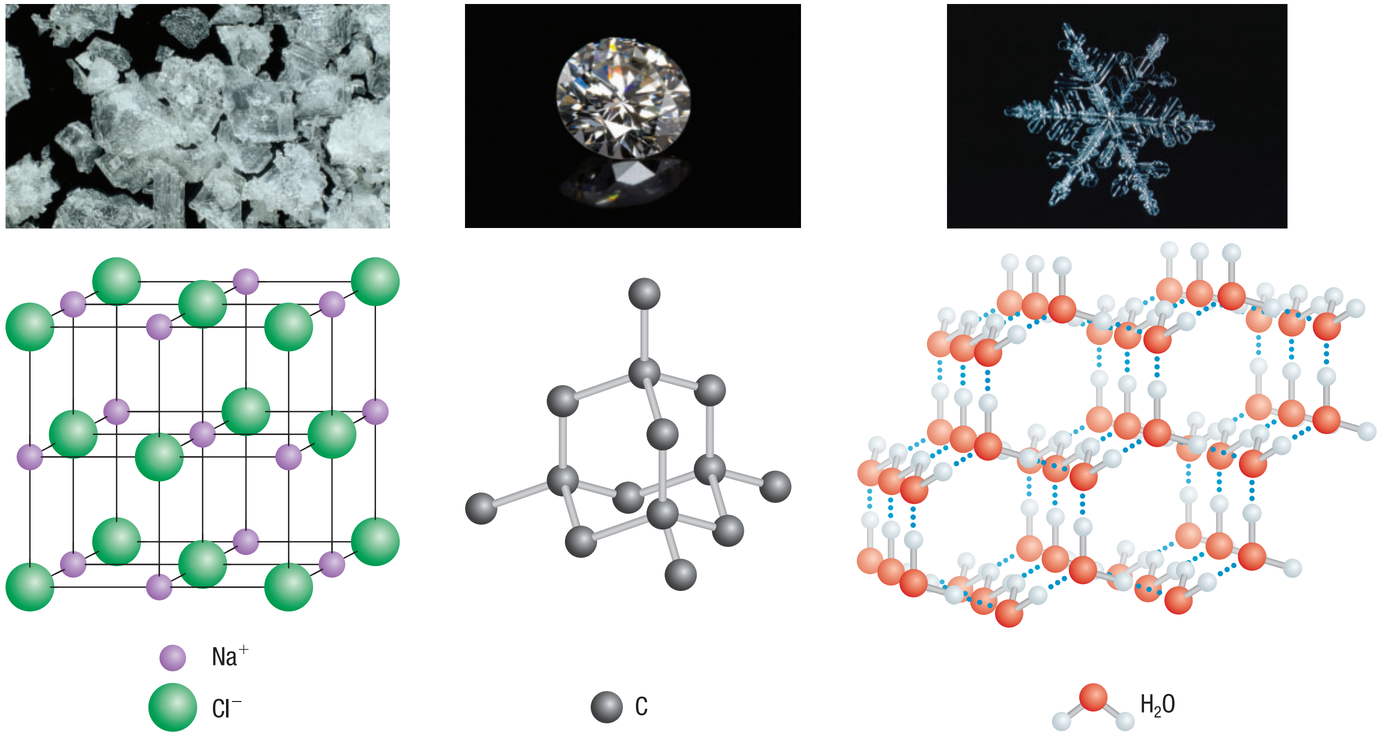
Figure 1 The Boeing 787 Dreamliner, made of composite materials, is more fuel-efficient than older aircraft.

composite material a material composed of two or more distinct materials that remain separate from each other in the solid phase

The rising cost of fuel has had a profound impact on the price we pay to travel. You are likely aware of how expensive gasoline is these days. Now imagine the cost of filling a commercial airplane's fuel tank, which is 3000 times larger than a car's gas tank! Given how much fuel an airplane consumes, it is not surprising that the cost of an airline ticket has increased substantially in recent years.

Because of high fuel prices, airplane designers have been working to develop lighter, quieter, and more fuel-efficient airplanes such as the Boeing 787 Dreamliner aircraft (**Figure 1**). This model of plane uses approximately 20 % less fuel than a comparable Boeing 767 model. The 787 Dreamliner is the first major airplane to use **composite materials**—materials made from 2 or more substances that have significantly different chemical and physical properties. In composite materials, the substances remain separate and distinct from each other. Many common products, such as boats, bricks, surfboards, and even concrete, use composite materials. The 787 Dreamliner is made of at least 50 % composite materials, being mostly carbon and reinforced plastic. This combination provides a high strength-to-weight ratio and makes the airplane lighter than other models. Composite materials are also resistant to corrosion, heat, and chemicals—ideal for high-atmosphere travel. The properties of a composite material are determined by the structural and bonding characteristics of the substances from which it is made.

In this section, you will learn about the structural and bonding characteristics of substances in the solid phase. There are many different types of solids, such as ionic solids, metallic solids, molecular solids, and network solids. These are all crystalline solids. **Figure 2** shows three types of crystalline solids. You can see that the structural properties of each solid are different from each other.



(a) sodium chloride **(b)** diamond **(c)** ice

Figure 2 Examples of the different types of crystalline solids. (a) Sodium chloride is an ionic solid composed of alternating sodium, Na^+, and chloride, Cl^-, ions. (b) Diamond is a solid arrangement of carbon atoms. (c) Ice is the solid form of water. The blue dotted lines show hydrogen bonds between adjacent polar water molecules.

Ionic Crystals

You are already familiar with ionic crystals because you have studied the ionic bond that forms between Na^+ and Cl^- ions. This ionic crystal forms from the interaction of metal (sodium) and non-metal (chloride) ions. The ions arrange in a crystal lattice structure, with alternating packing of the positive and negative ions (Figure 2(a)).

Many of the physical properties of NaCl(s) are also characteristic of other ionic crystals. For example, NaCl(s) is a hard, brittle solid. When it dissolves in water, the solution conducts electricity, but solid NaCl does not conduct electricity. Ionic crystals tend to have high melting points. Magnesium oxide (used in antacid tablets) is an ionic solid that has a melting point of 2852 °C. This property is the result of the strong ionic bonds that hold the oppositely charged ions together.

Metallic Crystals

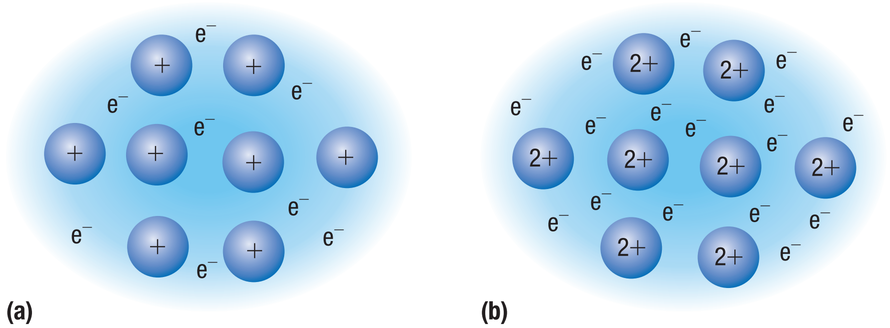
If you had the task of describing a metal, what words would you use? You might say that a metal is shiny or silvery. You may also describe a metal as a good conductor of thermal energy and electricity. In the solid state, metals form a **metallic crystal**, which is a structure composed of closely packed atoms held together by electrostatic interactions and free-moving electrons. Unlike ionic crystals, not all metallic crystals have similar properties. For example, solid gold is quite soft and easily moulded, making it useful in making jewellery. In contrast, solid aluminum, which is used to make items such as soft-drink cans, is much harder than gold so it keeps its shape better than gold. The melting points of metallic crystals also vary widely. Some metals, such as mercury, melt below room temperature, whereas others, such as tungsten, melt at temperatures higher than 3000 °C.

metallic crystal a solid with closely packed atoms held together by electrostatic interactions and free-moving electrons

What theory can explain these varied characteristics of metallic crystals? The **electron sea theory** postulates that metals are composed of closely packed atoms whose valence electrons are free to move. In this model, the positively charged nuclei of the atoms in the crystal remain at fixed points while the electrons are mobile (**Figure 3**). Imagine that you have placed several small marbles in a cup of water. The water (representing electrons) can move freely in the cup, but the marbles (representing nuclei) remain relatively fixed in place. The mobile electrons do not associate with 1 nucleus only, but move from nucleus to nucleus and thereby hold the positively charged nuclei together. This theory explains **metallic bonding**, the bonding that holds the nuclei and electrons of metals together.

electron sea theory a theory that states that the electrons in a metallic crystal move freely around the positively charged nuclei

metallic bonding the bonding that holds the nuclei and electrons of metals together



(a) **(b)**

Figure 3 In the electron sea model of metallic solids the electrons are mobile. (a) Model of the Group 1 alkali metals with 1 valence electron (b) Model of the Group 2 alkaline earth metals with 2 valence electrons

The electron sea theory explains several properties of metallic crystals. The atoms within metallic crystals have low ionization energies because they possess loosely held electrons that can move freely outside their valence orbitals. The strong forces of attraction between the positive nuclei and the electrons result in closely packed metallic crystal structures.

Table 1 lists examples of common properties of metallic solids and an explanation of these properties.

Table 1 Properties of Metallic Solids

Property	Explanation
sheen	Mobile valence electrons absorb and emit light energy of many wavelengths of light.
malleability	The "electron sea" allows atoms to slide over each other.
electrical conductivity	Mobile valence electrons produce an electric current when a metal is connected to a battery.
hardness	The "electron sea" surrounding the positive nuclei produces strong electrostatic attractions that hold the nuclei together.

Molecular Crystals

molecular crystal a solid composed of individual molecules held together by intermolecular forces of attraction

Some substances, called **molecular crystals**, form crystal lattice structures when in the solid state, including sulfur, iodine, water, and carbon dioxide. Molecular crystals are similar to ionic crystal lattices except that they are often more complex. For example, the molecular crystal of water (ice) can form several different types of structures in the frozen form. **Figure 4** shows a symmetrical hexagonal structure that is often the form of ice in a snowflake.

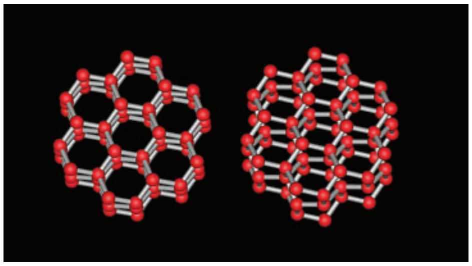


Figure 4 Two angles of the molecular model of a hexagonal lattice of solid water in a snowflake. In this illustration, atoms of both hydrogen and oxygen are red, covalent bonds between atoms are light grey, and hydrogen bonds between molecules are dark grey.

The intermolecular forces within a molecular crystal determine its structure and properties. Remember that intramolecular forces are much stronger than intermolecular forces. Intermolecular forces include London dispersion, dipole–dipole, and hydrogen bonding forces. Polar molecules exhibit both dipole–dipole forces and London dispersion forces, and non-polar molecules exhibit only London dispersion forces. The weak intermolecular forces help determine the properties of neutral molecules, which is why molecular crystals tend to have lower melting points and be less hard than ionic crystals. Molecular crystals contain neutral molecules, so they do not conduct an electric current very well, either in their pure form or in solution (**Table 2**). **Figure 5** shows a light micrograph of a crystal of iodine, $I_2(s)$, where molecules display a regular arrangement of equally spaced atoms within a lattice.

Table 2 Properties of Molecular Crystals

Property	Reason
low melting point	intermolecular interactions
little hardness	intermolecular interactions
electrical non-conductor	composed of neutral molecules

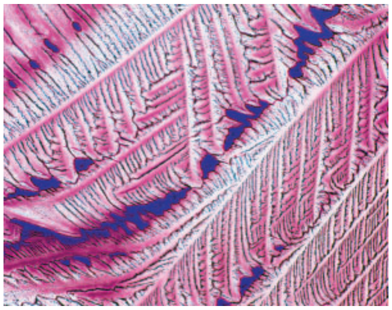


Figure 5 Polarized light micrograph of a crystal of iodine, I_2. The structure is a regular arrangement of iodine molecules.

Covalent Network Crystals

covalent network crystal a solid in which the atoms form covalent bonds in an interwoven network

A **covalent network crystal** is a solid in which the covalent bonds between atoms form an interwoven network. Diamond, the hardest naturally occurring substance on Earth, is an example of a covalent network crystal. The carbon atoms in a diamond molecule form a tetrahedral structure, as shown earlier, in Figure 2(b) on page 248. Each carbon atom forms 4 single covalent bonds to other carbon atoms by way of sp^3 hybrid orbitals. The network of covalent bonds is the source of the name for these crystals. You can predict some of the properties of covalent network crystals, using diamond as a model.

Covalent network crystals tend to have very high melting points and extreme hardness. The melting point of diamond is over 3500 °C. Therefore, the covalent bonding structure in a network solid must be very strong. You may have observed many hydrocarbon molecules that contain carbon–carbon covalent bonds, such as ethane and octane. The carbon–carbon bonds in diamond are no different than the carbon–carbon bonds in these molecules. However, the strength of diamond is a result of its interlocking network structure (**Figure 6**). Think of the strength of a braided rope. If you were to separate the individual strands, you would find that they are not very strong. Yet, when you braid the strands together, the rope is much stronger than any one strand.

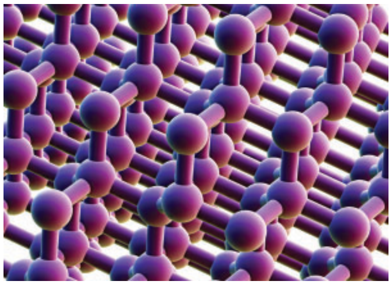
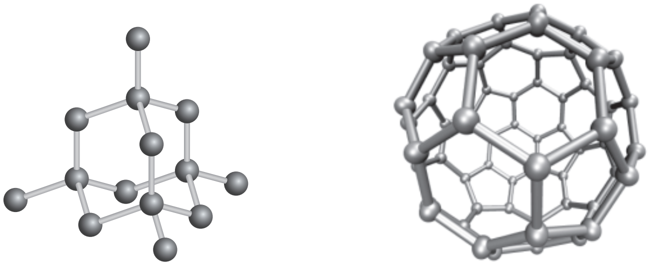


Figure 6 The covalent arrangement of carbon atoms in a solid diamond

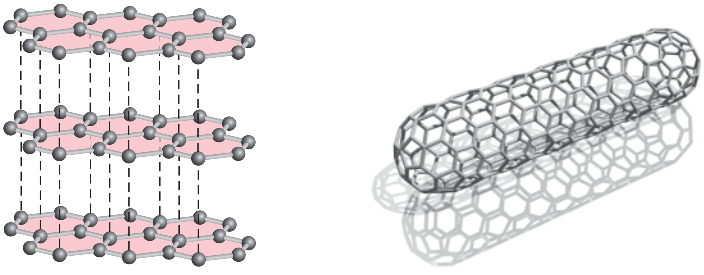
Since the atoms in diamond interlock, they do not move around easily. This accounts for the extreme hardness of covalent network crystals. A large amount of energy is required to break the bonds in a covalent network crystal and melt it. The electrons in covalent network crystals do not move freely through the crystal because the atoms and covalent bonds hold the electrons in place. Thus, covalent network crystals are not good conductors of electricity.

Carbon atoms can form other structures in addition to the structure found in diamond (**Figure 7(a)**). Carbon atoms can form layers or sheets when in the solid phase, such as in graphite (**Figure 7(b)**), large spherical molecules in buckyballs (**Figure 7(c)**), and long, thin carbon nanotubes (**Figure 7(d)**). WEB LINK



(a) diamond

(c) buckyball



(b) graphite

(d) carbon nanotube

Figure 7 The different structures of solid carbon. (a) The tetrahedral arrangement of carbon atoms in a diamond. (b) The layered sheet structure of carbon atoms in graphite. A weak bonding interaction occurs between the layers of carbon sheets. (c) The ring-like arrangement of carbon atoms in a buckyball (d) The long, tube-like structure of carbon atoms in nanotubes

Graphite has very different properties from diamond. Graphite is slippery, black, and an electrical conductor. These differences are a result of the difference in bonding within graphite. The carbon atoms arrange in a hexagonal sheet. Each carbon atom in a sheet of graphite bonds to 3 other carbon atoms in a trigonal planar arrangement. Therefore, electrons in sp^2 hybrid orbitals form the covalent bonds in graphite. This arrangement results in delocalized electrons in *p* orbitals that can move from one side of the sheet to the other, which accounts for the electrical conductivity of graphite. Graphite has strong covalent bonds along the plane of the graphite sheet, and weaker London dispersion forces hold the graphite layers together (Figure 7(b)).

buckyball a spherical arrangement of carbon atoms that forms a hollow, cage-like structure

carbon nanotube a solid made of carbon atoms similar to graphite rolled into a cylinder

A **buckyball** consists of 60 carbon atoms arranged in a soccer ball–like structure. Its actual name is buckminsterfullerene, in honour of Richard Buckminster Fuller, who built architectural domes of this shape. The carbon atoms link together to form a hollow, dome-shaped cage. Buckyballs are extremely stable structures that have very high melting points. In the past 15 years, buckyballs have become popular because they have many different applications. Uses for buckyballs include chemical sensors, photovoltaic cells, cosmetics, and vehicles for delivering pharmaceutical drugs to cells. **Carbon nanotubes** are very similar in structure to buckyballs except that they have a cylindrical shape that is rolled at specific angles. The properties of nanotubes differ depending on their circumference, length, and twist. Nanotubes were discovered in 1991, and scientists are still learning more about the properties and applications of these structures.

Most covalent network crystals comprise the elements and compounds of carbon and silicon. The element silicon belongs to the same group (Group 14) as carbon in the periodic table. Silicon compounds make up most rocks, sand, and soil found on Earth. Crystalline quartz is a covalent network crystal of the silica molecule, SiO_2 (**Figure 8(a)**). Quartz forms a regular structure of molecules within the crystal.

When you heat solid silica above its melting point and then cool it rapidly, solid glass forms. Glass has a much more disordered structure than quartz (**Figure 8(b)**). Cooling molten glass quickly forms a structure that is not crystalline. In fact, glass more closely resembles a very viscous liquid than it does a crystalline solid. The properties of glass can change depending on the addition of different additives. For example, borosilicate glass, made of boron oxide and silica, produces a glass that does not expand or contract much when its temperature changes. Borosilicate glass is commonly used in labware and cookware because it resists breaking when heated or cooled rapidly.

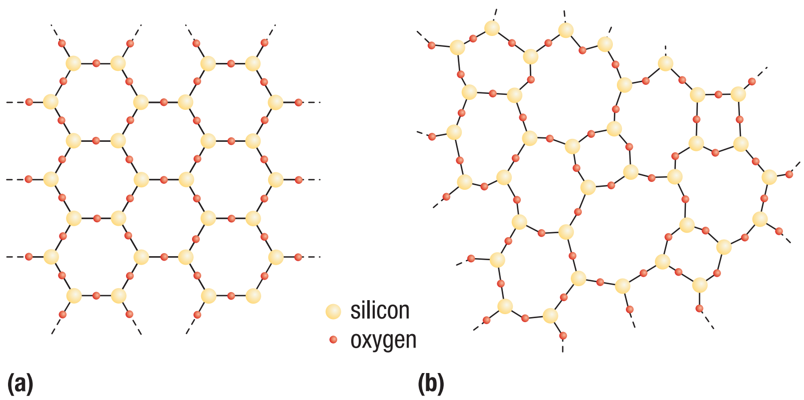


Figure 8 Two-dimensional representations of (a) a quartz crystal and (b) quartz glass. Note the irregular structure of the glass in contrast to the regular structure in the crystal.

semiconductor a substance that conducts a slight electric current at room temperature but has increasing conductivity at higher temperatures

Semiconductors

Transistors are essential components of electronic devices. As transistors have decreased in size, so has the size of electronic devices, while the capabilities of these devices have increased. You can listen to music, work at a computer, and watch television because of transistors. Transistors act as amplifiers and switches in electronic circuits. Semiconductors are essential components of transistors. **Semiconductors** consist of covalent crystals of elements such as silicon or germanium that conduct a small amount of electric current in standard conditions. When you increase the temperature slightly, the conductivity increases significantly. Engineers modify silicon or germanium by adding a small amount of an element such as arsenic or boron in a process called doping. This process allows engineers to create semiconductors with specific conductive properties (**Figure 9**).

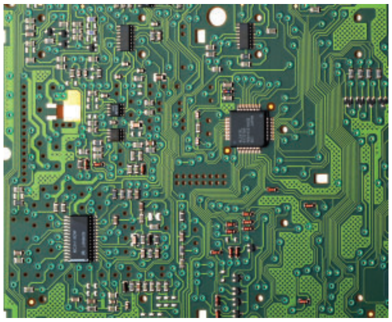


Figure 9 This microchip, which can contain millions of transistors, is built on a wafer of semiconductor material.

The atoms in a semiconductor have full valence electron shells, so electrons do not move from one atom to another. Thus, semiconductors are normally nonconductors. Semiconductors are sometimes doped with arsenic, which has 1 more valence electron than silicon. A slight increase in temperature causes these additional electrons in arsenic to jump to a higher energy level. When the electrons are in an excited state, they move from atom to atom easily and the semiconductor's conductivity increases (**Figure 10(a)**). This type of semiconductor is an n-type semiconductor. Silicon can also be doped with boron, which has 1 less valence electron than silicon. The missing electron creates a hole around the boron atoms that electrons from surrounding atoms move to fill, which also increases the semiconductor's conductivity (**Figure 10(b)**). This type of semiconductor is a p-type semiconductor.

CAREER LINK

Investigation **4.8.1**

Identifying Solids (page 259)
Now that you know about the different types of solids, perform Investigation 4.8.1 to identify solids based on their physical and chemical properties.

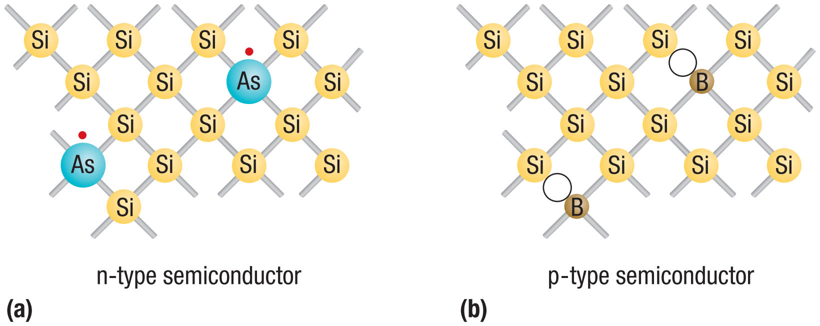


Figure 10 (a) A silicon crystal can be doped with arsenic, which has one more valence electron than silicon. (b) A silicon crystal can also be doped with boron, which has one less valence electron than silicon.

Research This

3-D Photocopiers

Skills: Researching, Analyzing, Evaluating, Communicating

SKILLS HANDBOOK A5.1

Imagine that you are building a small bird feeder at home and you run out of nails. Typically, you would go to the store to purchase the nails. Now suppose you had a 3-D photocopier, or "fabricator"—a futuristic machine able to reproduce any three-dimensional object. Instead of going to the store, you could just reproduce the nails at home with the touch of a button. This idea may sound like science fiction to you, but scientists and engineers are beginning to develop such a machine (**Figure 11**).

Figure 11 A 3-D photocopier may one day allow you to create any object. Just design the object that you need from your computer and in a matter of seconds, a real-life replica is produced.

To design a machine like this, it is important to understand the structure of the atoms and molecules that comprise these objects, because this technology would rely on the concepts of chemical bonding and the structure of matter. Although the reality of such a machine may be many years into the future, the concept is interesting and a good topic of conversation.

1. Research 3-D photocopiers to find out the latest progress in their development.

A. In what ways could this machine change your life? A

B. What type of object do you think you would 3-D photocopy most often? A

C. What types of objects would be most difficult to 3-D photocopy? A

D. Are there any objects that you could not make with this machine? A

E. How could this machine promote green chemistry? A

F. Describe any drawbacks to using such a machine. A

WEB LINK

4.8 Review

Summary

- The four types of solids are ionic crystals, metallic crystals, molecular crystals, and covalent network crystals.
- Ionic crystals form when a metal reacts with a non-metal, producing oppositely charged ions that are electrostatically attracted to each other. An example of an ionic crystal is sodium chloride.
- Metallic crystals are bound by a sea of electrons. This region of negative charge explains the electrical conductivity, hardness, and flexibility of metals. An example of a metallic crystal is aluminum.
- The properties of molecular crystals are in part determined from the intermolecular dipole–dipole and hydrogen bonding forces in these substances. Lower melting points, less hardness, and electrical non-conductivity are characteristics of molecular crystals. Ice is an example of a molecular crystal.
- Hardness, electrical non-conductivity, and high melting point are characteristics of covalent crystals. Diamond is an example of a covalent crystal.
- Semiconductors are often made of silicon or germanium. Engineers modify silicon or germanium by doping it with a small amount of an element such as arsenic or boron.

Questions

1. Make a chart summarizing the properties of the four types of solids. Use the following headings: K/U C
    - Type of solid
    - Particles involved
    - Primary force of attraction
    - Boiling point
    - Electrical conductivity: solid, liquid, solution
    - Other physical properties of crystal
    - Conditions necessary for formation
    - Examples
2. Predict the type of solid that you would expect to have each of the following characteristics: K/U
    (a) greatest electrical conductivity
    (b) lowest melting point
    (c) highest conductivity when dissolved in water
    (d) lowest hardness
3. Provide an explanation for each of your answers in Question 2. K/U
4. Compare and contrast the structures of the following solids: K/U
    (a) $CO_2(s)$ versus $H_2O(s)$
    (b) NaCl(s) versus HCl(s)
5. Explain what the term “doping” means and why engineers dope semiconductor materials. K/U
6. What type of solid is a substance that
    (a) conducts electricity and has a high melting point?
    (b) does not conduct electricity as a solid but does when dissolved in water?
    (c) does not conduct electricity and has a high boiling point?
    (d) does not conduct electricity and has a low boiling point? K/U
7. Suggest a method to distinguish each of the following pairs of solids: T/I A
    (a) ionic crystal, molecular crystal
    (b) metallic crystal, covalent crystal
    (c) molecular crystal, metallic crystal
    (d) ionic crystal, covalent crystal
8. Explain how you could tell experimentally if titanium dioxide, TiO_2, is an ionic solid or a molecular solid. K/U T/I A
9. Switching salt and sugar on a table is a common prank. Since both substances look alike, they can be switched easily. Despite their similar appearance, salt and sugar differ in their properties because one is a molecular solid and the other is an ionic solid. Explain how and why their properties are different. K/U T/I A