Classroom Photocopying Permission

Chapters from Teaching General Chemistry: A Materials Science Companion. Copyright © 1993 American Chemical Society. All Rights Reserved.
For reproduction of each chapter for classroom use, contact the American Chemical Society or report your copying to the Copyright Clearance Center, Inc., 222 Rosewood Drive, Danvers, MA 01923.

Experiments from Teaching General Chemistry: A Materials Science Companion. Copyright © 1993 American Chemical Society. All Rights Reserved. Multiple copies of the experiments may be made for classroom use only, provided that the following credit line is retained on each copy: "Reproduced with permission from *Teaching General Chemistry: A Materials Science Companion*." You may edit the experiments for your particular school or class and make photocopies of the edited experiments, provided that you use the following credit line: "Adapted with permission from *Teaching General Chemistry: A Materials Science Companion.*"

Overhead Masters
Multiple copies of the overhead masters may be made for classroom use only, provided that the extant credit lines are retained on each copy: "© 1993 American Chemical Society. Reproduced with permission from *Teaching General Chemistry: A Materials Science Companion*" or "© 1995 by the Division of Chemical Education, Inc., American Chemical Society. Reproduced with permission from *Solid-State Resources* ."

Laboratory Safety

DISCLAIMER

Safety information is included in each chapter of the Companion as a precaution to the readers. Although the materials, safety information, and procedures contained in this book are believed to be reliable, they should serve only as a starting point for laboratory practices. They do not purport to specify minimal legal standards or to represent the policy of the American Chemical Society. No warranty, guarantee, or representation is made by the American Chemical Society, the authors, or the editors as to the accuracy or specificity of the information contained herein, and the American Chemical Society, the authors, and the editors assume no responsibility in connection therewith. The added safety information is intended to provide basic guidelines for safe practices. Therefore, it cannot be assumed that necessary warnings or additional information and measures may not be required. Users of this book and the procedures contained herein should consult the primary literature and other sources of safe laboratory practices for more exhaustive information. See page xxv in the Text 0 Preface file in the Companion Text folder for more information.

Chapter 10

Synthesis of Materials

The materials tetrahedron of Chapter 1 and the examples of materials in other chapters underscore the special synthetic opportunities and challenges posed by solids: The desired properties of a material or of an interface derived therefrom can be dependent not only on stoichiometric considerations, but on features like atomic-scale defects and microstructure, which are influenced by processing. For example, tangled dislocations cause copper to be more mechanically robust (work hardening, Chapter 6); parts per million of impurity atoms drastically alter the electrical conductivity of semiconductors (doping, Chapter 8); and the concentration of oxygen vacancies controls electromagnetic properties (perovskite superconductivity, Chapter 9).

Nowhere is the vitality of materials chemistry more evident than in our emerging ability to control the arrangement of atoms from the nanoscale to the macroscale. This chapter is intended to provide some context for the synthetic revolution that is the foundation for the Age of Materials.

The first part of the chapter provides the rationale for, and examples of, the traditional, high-temperature, brute force approach to making solids react with one another. Precursor strategies that can be used to coax reactants to form the desired products under milder conditions are presented as well. The second and third parts of the chapter focus on solvent- and gas-phase-based synthetic strategies. These versatile techniques are being used to prepare a broad range of technologically important materials that include diamond films, glass optical fibers, and the multilayered structures of semiconductor diode lasers. In some instances atomic-scale synthetic control can be achieved. Finally, techniques are described for carrying out chemistry inside certain host crystal structures and for preparing large, high-purity crystals of technological importance.

2725-X/93/0329$07.00/1

© 1993 American Chemical Society

Solid-Phase Techniques

Diffusion and "Heat-and-Beat" Methods

Many solid-state syntheses are based simply on heating a mixture of solids together with the intent of producing a pure, homogeneous sample of desired stoichiometry, grain size, and physical–chemical properties. These reactions depend on the ability of atoms or ions to diffuse within or between solid particles, Figure 10.1. Diffusion is typically many orders of magnitude slower in solids than in the liquid or gas phases; therefore, high temperatures are required for the reaction to proceed on a reasonable time scale.

Laboratory. Experiment 13 investigates the relative rates of diffusion of gases, liquids, and solids.

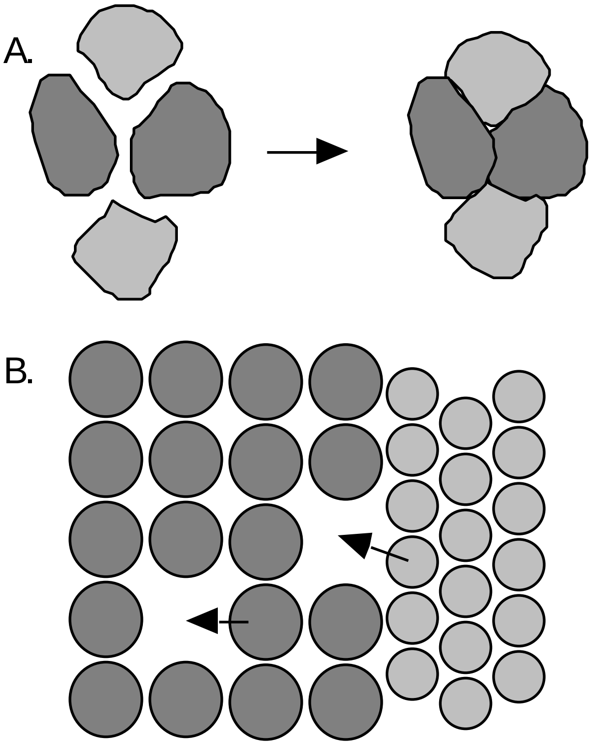


Figure 10.1 What the "heat and beat" methods accomplish. A. Precursor particles are brought into close contact. B. Atoms intermingle by diffusion through vacancies or interstitial positions (*see* Chapter 6).

A dramatic illustration of these principles is provided by the reaction of either nickel or cobalt with aluminum to produce the intermetallic compounds CoAl or NiAl, which have the CsCl structure (Chapter 5; the high-temperature phase of NiTi "memory metal," Chapter 9, also has this structure). Bars of these metal mixtures are easily made, using a die to compact the metal powders and a standard press. The bar requires ignition by sustained exposure of one of its ends to a very hot propane torch. Once ignited, the reaction is sufficiently exothermic (the temperature likely exceeds 1500 °C and may cause localized melting) that it is self-sustaining: the bright orange reaction front travels along the bar with the visual impact of a controlled thermite reaction! Figure 10.2 helps appreciate the extensive shuffling of atoms that has to accompany the conversion of the starting materials, which have the fcc crystal structure, to the CsCl structure of the products. A more quantitative perspective on this kind of atomic shuffling is given in the discussion of the synthesis of the superconducting 1-2-3 compound later in the next section.

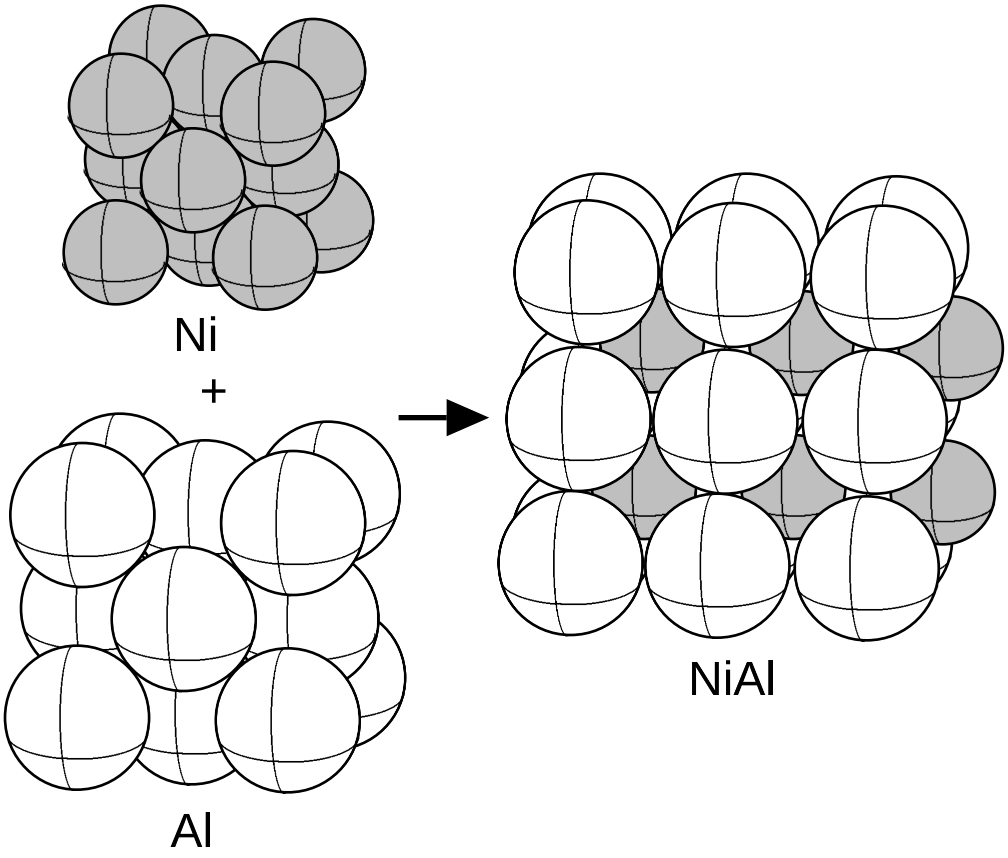


Figure 10.2. Elemental Ni and Al have the face-centered cubic structure, and NiAl has the CsCl structure.

Demonstration 10.1 Synthesis of NiAl and CoAl

Caution: The reaction is vigorously exothermic. Keep a safe distance after initiating the reaction and make sure viewers are at a safe distance of at least several meters. Make sure that all flammable materials have been removed from the demonstration area. Conduct this demonstration with the level of caution used for thermite reactions *(1)*.

Materials

325-mesh elemental powders (aluminum and nickel or cobalt)
A die in which to compact the powders (*see* text and Figure 10.3)
A press (a press used for making KBr pellets for infrared spectra, such as a Carver laboratory press, is suitable)
Lithium stearate
Fire brick (or other surface able to withstand temperatures on the order of 2000 °C)
Propane torch
Fire extinguisher

Procedure

- Weigh out correct molar ratios of aluminum and cobalt, or aluminum and nickel, in order to form CoAl or NiAl. A total mass of 8 g will be sufficient for a mold the size of the one described in Figure 10.3. On this scale, use 5.49 g of Co and 2.51 g of Al to make CoAl; or 5.48 g of Ni and 2.52 g of Al to make NiAl. **Caution: Avoid inhalation of airborne metal particles and direct contact with the powders. Wear a mask and gloves when dispensing and weighing the powders.**
- Place the powders in a sealed container of glass or plastic and shake vigorously.
- Coat a suitable die with lithium stearate to prevent the aluminum from cold-welding to the steel. A die can be manufactured from a stainless steel bar and bolts (*see* Figure 10.3). Lithium stearate can be synthesized by mixing 1:1 molar ratios of a solution of stearic acid in ethanol with an aqueous solution of lithium hydroxide.
- Place the powder evenly in the die and press at 20,000 lbs for a few minutes. Carefully remove the fragile bar from the die.
- Place the pressed bar on a fire brick and heat one end of the bar with a propane torch, using the hottest part of the flame (just above the blue cone). Once the edge begins to glow orange (this may take a minute or two), remove the torch. If the reaction does not proceed, try the other end of the bar.
- The product is much less magnetic than the original mixture.

Figure 10.3. Diagram of the center bars and body of the die (actual size) described in Demonstration 10.1. All components are made out of 1/4-inch square stainless steel rods. (The center bars are of the correct length to just fit in the gap in the center of the body of the die.) Holes are drilled through the six bars forming the body, and small nuts and bolts are used to secure the pieces as shown. The body of the die is placed on a piece of cardboard that has a hole cut in it that is the shape of one of the center bars. A center bar is pushed through the hole in the die body and into the hole in the cardboard. In this way, the body of the die is held above the center bar. The cardboard and center bar will rest on the counter (or, on the base of the press). The powder may then be placed on the center bar. The second center bar is then placed on top of the powder. When the press is used, the powder is squeezed between the two center bars. After releasing the pressure, the pressed sample may be removed from the die by carefully removing the top center bar and loosening the bolts.

The reaction of aluminum with nickel or cobalt typifies many aspects of reactions between solids: It is often necessary to heat finely ground, intimate mixtures of solids to temperatures of the order of 1000–1500 °C in order to enhance the rates of diffusion between the reactants. In many syntheses, several cycles of heating for many hours, each followed by regrinding at room temperature, and a final heating may be needed to form a homogeneous sample. With the elevated temperatures and extended times used in such reactions, the products are usually the thermodynamically stable phases (or mixtures of phases); compounds that are stable only at relatively low temperatures may be inaccessible by this synthetic approach.

The preparation of the 1-2-3 superconductor $YBa_2Cu_3O_{7-x}$, described in Experiment 11, is another example of high-temperature synthesis. Samples of $YBa_2Cu_3O_{7-x}$ can be prepared by heating a finely ground, well-mixed powder, consisting of a stoichiometric mixture of Y_2O_3, BaO_2 (or $BaCO_3$), and CuO, at about 950 °C. After heating, the sample is reground and pressed into a pellet and reheated (sintered; described later in this section) at 950 °C. Following sintering, the pellet is heated in an atmosphere of pure oxygen at 500–600 °C, then slowly cooled to room temperature. Each of the steps in this process addresses problems that can arise during a solid-state synthesis.

The necessity for heating finely ground and well-mixed precursor compounds in this synthesis is attributable to the structures of the starting materials and products. In $YBa_2Cu_3O_{7-x}$ all three metal ions are mixed on an atomic scale; particles of the starting materials each contain only one type of ion. Thus, yttrium, barium, and copper ions must all diffuse together in order for the 1-2-3 product to form.

Extensive grinding in a mortar and pestle produces particles with a radius of about 10^{-3} cm. Copper ions are separated by about 4×10^{-8} cm in the particles of CuO; thus about 25,000 copper ions are along the line between the ions in the center of these particles and the surface of the particle. If, for example, yttrium and barium ions are to diffuse into the center of the particle, these ions must push their way past thousands of other positive ions that lie between the surface and the interior of the particle. This process is slow and requires activation by heating.

Regrinding the sample exposes unreacted portions of the reactants. Pressing a pellet increases the contact between the surfaces of the particles that compose the sample. Thus regrinding and pelletizing helps to ensure complete reaction. Subsequent sintering (heating to temperatures a little below the melting point) promotes bonding between the grains that compose the pellet, thereby increasing the density and mechanical strength of the pellet. Sintering is somewhat like forming a snowball in that it is easier to get the snow to stick together if it is near the melting point of ice. For a snowball, squeezing the snow in one's hands helps to increase the snowball's density by fusing grains of snow; this is like pressing a pellet of a solid-state sample before heating.

The oxidation states in many solids that contain ions that can exhibit two or more oxidation states can be controlled by varying the oxidizing or reducing character of the atmosphere above the substance. As discussed in Chapter 9, annealing $YBa_2Cu_3O_{7-x}$ in a pure oxygen atmosphere increases the percentage of ions that are formally Cu(III) in the sample.

Precursor Techniques

In the synthetic technique just described, the reactants are finely divided and mixed manually to produce as intimate a mixture as possible. It is sometimes possible to improve mixing by preparation of a precursor (generally by precipitation from solution) that will contain the reactants in a mixture with atomic scale mixing. These precursors are reactive at lower temperatures and require shorter heating times than mechanically mixed samples of solids: Because the reactant atoms or ions are mixed at the atomic, or near atomic level, in the precursor, the distances that they need to diffuse during reaction are much smaller than between solid particles.

In many cases the precursor is simply a finely divided, coprecipitated, solid mixture or a gelatinous mass called a gel. For example, yttrium iron garnet, $Y_3Fe_5O_{12}$, can be prepared by the reaction of a stoichiometric mixture of finely divided, well-mixed Y_2O_3 and Fe_2O_3 at 1100 °C.

$$3\ Y_2O_3 + 5\ Fe_2O_3 \rightarrow 2\ Y_3Fe_5O_{12} \qquad (1)$$

However, the reaction proceeds much more rapidly and at about 900 °C if a precursor consisting of a stoichiometric solid mixture of $Y(OH)_3$ and $Fe(OH)_3$ is used. This mixture is prepared by coprecipitation of the hydroxides from an aqueous solution of stoichiometric amounts of soluble salts of Y^{3+} and Fe^{3+}.

$$3\ Y^{3+}(aq) + 5\ Fe^{3+}(aq) + 24\ OH^{-}(aq) \rightarrow \\ 3\ Y(OH)_3 / 5\ Fe(OH)_3\ (s, mixture) \qquad (2)$$

$$3\ Y(OH)_3 / 5\ Fe(OH)_3\ (s, mixture) \xrightarrow{heat} Y_3Fe_5O_{12}\ (s) + 12\ H_2O \qquad (3)$$

Laboratory. Experiment 14 describes the synthesis and magnetic studies of yttrium iron garnets prepared from a co-precipitated precursor.

Stoichiometric control can sometimes be improved if a single compound serves as a precursor. For example, the perovskite (Chapter 5) $LaCoO_3$ is readily prepared from compounds that contain the cobalt and lanthanum ions mixed on an atomic scale in a 1:1 ratio. One such compound is $La[Co(CN)_6]$, which forms as a hydrated precipitate from the reaction between a solution of a lanthanum salt and a solution of $K_3[Co(CN)_6]$. This compound can be converted to $LaCoO_3$ by heating in air for a short time.

$$LaCl_3(aq) + K_3[Co(CN)_6]\ (aq) \rightarrow La[Co(CN)_6]\cdot xH_2O(s) + 3\ KCl(aq) \qquad (4)$$

$$2\ La[Co(CN)_6]\cdot xH_2O(s) + 15\ O_2\ (g) \xrightarrow{heat} \\ 2\ LaCoO_3(s) + 12\ CO_2(g) + 6\ N_2(g) + 2x\ H_2O(g) \qquad (5)$$

A variety of other solid mixtures and stoichiometric compounds also can be used as precursors. For example, mixtures of iron(III) and zinc oxalates readily decompose to form $ZnFe_2O_4$, a compound with the so-called spinel structure.[1] A zinc chromium spinel, $ZnCr_2O_4$, which is used as a magnetic recording medium in cassette recorders, results from the decomposition of the stoichiometric compound ammonium zinc chromate, $(NH_4)_2Zn(CrO_4)_2$.

$$(NH_4)_2Zn(CrO_4)_2\ (s) \xrightarrow{heat} ZnCr_2O_4(s) + N_2\ (g) + 4\ H_2O\ (g) \qquad (6)$$

---

[1] In the spinel ($MgAl_2O_4$) structure, the oxide ions are in a ccp array with the Mg^{2+} ions in tetrahedral holes and Al^{3+} in octahedral holes.

In principle, coprecipitation and other precursor methods should be applicable to a wide variety of syntheses. However, the reaction conditions usually must be worked out on a case-by-case basis.

Reactions in Liquids

Solvents

Significant advantages are gained by conducting a reaction in a liquid medium: Diffusion rates are much faster in liquids, and the liquid phase can be more readily stirred to enhance mixing. Techniques involving liquids in the synthesis of solids include dissolving reactants in water or other solvents at relatively low temperatures, using molten salts or molten metals as solvents (called fluxes) at moderately high temperatures, and using reactants or products as the molten medium. The formation of lead iodide from lead nitrate and potassium iodide or sodium iodide illustrates the ability of a solvent to enhance reactivity.

Demonstration 10.2. Solvent Influence on Reactivity

Materials

1 g of lead(II) nitrate
1 g of potassium iodide or sodium iodide
Dry test tube and stopper
Water

Procedure

- Place about 1 g of lead(II) nitrate and 1 g of potassium iodide or sodium iodide in a ***dry*** test tube and shake. At best, only a faint tinge of yellow–orange color will be observed on the surface of the powders.
- Add several milliliters of water, and a brightly colored yellow–orange precipitate of lead iodide will form immediately.

Caution: Lead compounds are toxic. Avoid skin contact and inhaling dust from the compounds. Place the waste from this demonstration in an appropriately labeled container and dispose of it according to state and local regulations.

Some solids are prepared from aqueous solution. For example, crystals of alum and Cr-doped alums (Experiment 3) can be grown by direct precipitation from water. Preparation from solution does not require that the reactants be extensively soluble in the solvent. For example, as may be observed in Experiment 12, the ionic conductor Cu_2HgI_4 forms when

HgI_2 and CuI, both of which are only slightly soluble, are heated together in water.

$$HgI_2 + 2\ CuI \rightarrow Cu_2HgI_4\,(s) \qquad (7)$$

An important application of synthesis from an aqueous solution is the preparation of molecular sieve zeolites. Zeolites (Chapter 5) are aluminosilicates that have a framework of tetrahedral silicate and aluminate units arranged to form large tunnels and cavities. The tunnels are hydrated and contain additional cations necessary for the electroneutrality of the solid. Dehydrated zeolites can selectively absorb small molecules into the tunnels, and many are catalysts with extensive industrial applications. Most zeolites decompose above about 400 °C, so their synthesis must be accomplished at lower temperatures.

The starting materials for zeolite synthesis are solutions of salts of silicate and aluminate anions in aqueous alkali. Upon mixing, a gel forms from the coprecipitation of the silicate and aluminate anions. Subsequent heat treatment (sometimes under high pressure at temperatures above the normal boiling temperature of water––a so-called hydrothermal treatment) increases the solubility of the gel, and crystals of zeolite are produced from the resulting solution. The process may be represented as follows *(2)*:

$$x\mathrm{NaAl(OH)_4(aq)} + y\mathrm{Na_2SiO_3(aq)} + \mathrm{NaOH(aq)} \xrightarrow{25\ ^\circ\mathrm{C}} \mathrm{gel} \qquad (8)$$

$$\mathrm{gel} \xrightarrow{25\,-\,175^\circ\mathrm{C}} [\mathrm{Na}_x(\mathrm{AlO_2})_x(\mathrm{SiO_2})_y\cdot m\mathrm{H_2O}]\ (\text{zeolite crystal}) \qquad (9)$$

Nonaqueous solvents can also be used to advantage in the synthesis of solid-state materials. Organometallic precursors that are soluble in organic solvents can be used to produce extended solids. For example, a zerovalent nickel compound, L_2Ni, reacts with an alkylphosphine and alkylphosphine telluride in boiling toluene over a period of several hours to produce a polycrystalline precipitate of NiTe in quantitative yield *(3)*. In contrast, the direct reaction of the elements requires heating at 400–600 °C for days to weeks in order to produce NiTe.

$$R_3P + L_2Ni + R_3PTe \rightarrow NiTe + 2R_3P + 2L \qquad (10)$$

An additional advantage to this route is that by varying the reaction stoichiometry, intermediate metal clusters can be isolated.[2] Clusters may be viewed as model compounds for extended solids, and studying them can provide insight into the mechanism by which the bulk solids form from the reaction of soluble organometallic compounds. Furthermore,

---

[2] A metal cluster is a compound that has more than two metal atoms in close proximity, but fewer than the number of atoms required to give the properties of a bulk metal. In this particular case, clusters of the general formula $Ni_9Te_6L_8$ and $Ni_{20}Te_{18}L_{12}$ can be isolated.

clusters have different properties than the related extended solids and are interesting materials in their own right.

Melts (Fluxes)

Chemists typically recrystallize molecular compounds by dissolving them in a hot solvent, then allowing them to reprecipitate upon cooling. Solid-state chemists do likewise, except they usually use molten salts rather than lower boiling solvents. For example, crystals of yttrium iron garnet, $Y_3Fe_5O_{12}$, can be produced by dissolving a sample of the garnet in a molten mixture of PbO and PbF_2, followed by slow cooling. The solidified melt is removed from the crystals by dissolving it in acetic acid, in which the garnet is insoluble.

Melts can also be used as solvents for synthesis. Liquid tin (m.p. 232 °C) is used as a solvent for the reaction of ruthenium and phosphorus, producing RuP_2; and molten copper (m.p. 1083 °C) is used as a solvent for the production of MnSi from manganese and silicon.

An interesting technique that can be used for either synthesis or crystal growth is to have the reactants serve as both solvent and container. Many oxides can be prepared in this fashion. For example, $LaTiO_3$ can be prepared from a mixture of molten La_2O_3 and Ti_2O_3. However, this reaction requires extremely high temperatures (La_2O_3 melts at 2315 °C; Ti_2O_3 at 2130 °C) and exotic containers that neither react with the melt nor themselves melt at extremely high temperatures. One way to handle the problem is to create a solid shell (or skull) of the reactants that acts as a sample container. This step can be accomplished by placing a mixture of the reactants in a copper block that is cooled by water passing through tubes in the block, and heating the sample with an electric arc (similar to that of an arc welder) or with an extremely powerful microwave source. The portion of the sample in contact with the cool block does not melt and forms a solid shell that contains the remainder of the sample, which is molten. The molten reactants form product and, after cooling, the crystalline product is recovered by cutting away the skull.

Gas-Phase Synthesis

Chemical Vapor Transport

Arguably, no synthetic technique in the past 20 years has had a greater impact on materials science than chemical vapor methods. Several common examples are presented in this section.

The growth of large, pure single crystals is facilitated by a method called chemical vapor transport. This technique generally involves an equilibrium between solid and gaseous reactants and their gaseous reaction products. The growth of large single crystals of ZnS from microcrystalline ZnS is an example of the process.

At elevated temperatures, solid ZnS reacts with gaseous iodine to establish an equilibrium with gaseous diatomic sulfur and gaseous zinc iodide.

$$\mathrm{ZnS(s)} + \mathrm{I_2(g)} \rightleftarrows \mathrm{ZnI_2(g)} + 1/2\ \mathrm{S_2(g)} \qquad (11)$$

This reaction is endothermic. If equilibrium is established at 900 °C, cooling the mixture to 800 °C will shift the equilibrium to the left, producing crystalline ZnS.

The reaction is generally run in a sealed tube (Figure 10.4) with microcrystalline ZnS at one end at 900 °C and the empty end of the tube at 800 °C. As ZnS reacts, the gases, which are at equilibrium at 900 °C, diffuse down the tube to the cooler end, where the equilibrium conditions are different, and ZnS reforms, generally as single crystals. Equilibrium is maintained at either end of the tube because the reaction of ZnS and its deposition are faster than the rate of diffusion of gases through the tube. Generally, transport rates are low and only a few milligrams per hour are deposited. However, as is typically the case when crystals are grown slowly, the crystals that form are usually quite large and of very high quality.

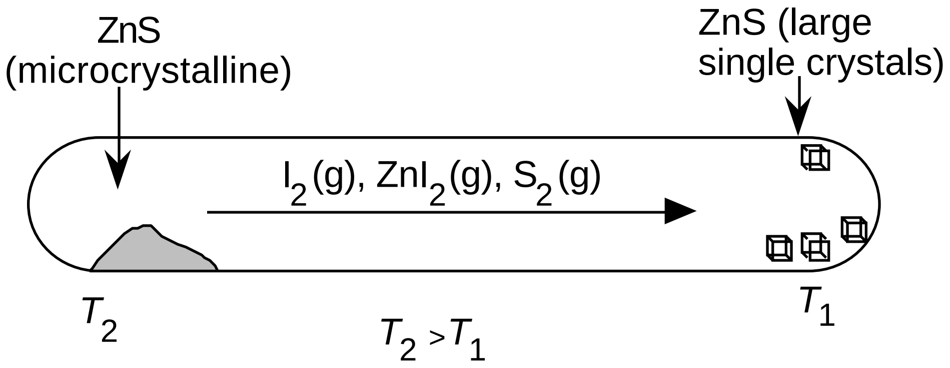


Figure 10.4. The arrangement of reactants, products, and temperatures for the chemical vapor transport of zinc sulfide. (Adapted with permission from reference 2.)

Chemical vapor transport can also be used for synthesis. For example, Cu_3TaSe_4 can be prepared by the reaction of Cu, Ta, and Se at 800 °C in a transport tube containing a little iodine: crystals of Cu_3TaSe_4 form at 750 °C in the cooler end of the tube.

Preparation of Thin Films

Metals can be evaporated from a target in vacuum by ion bombardment, electron bombardment, or heating (Figure 10.5). The evaporated metals condense on a substrate and its surroundings as a film. The thickness of the film depends on the rate of evaporation of the metal and the length of the exposure to the vapor. With experience, films only several atoms thick can be applied, and sandwich structures, consisting of alternating layers of different metals, can be deposited onto the substrate.

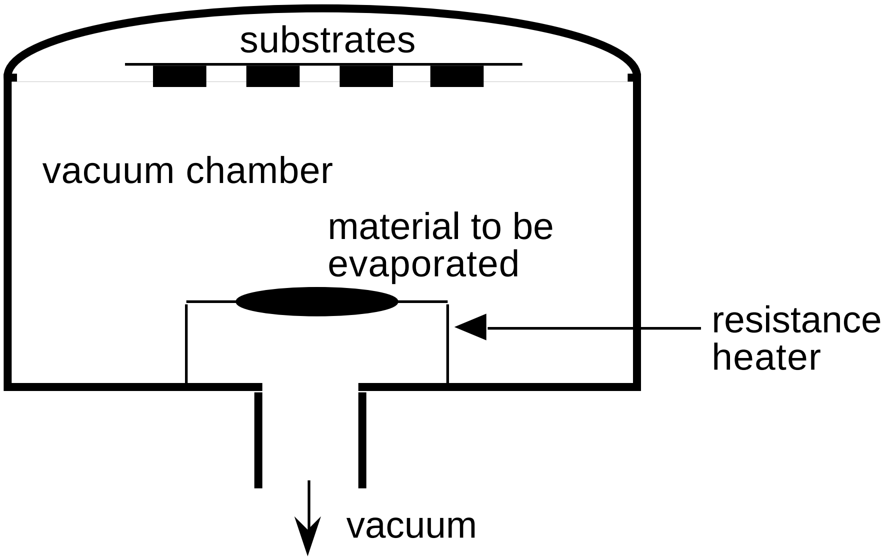


Figure 10.5. Vacuum evaporation equipment for thin film deposition. Atoms evaporate from the source as it is heated and deposit on the substrates. (Adapted with permission from reference 2.)

Evaporation of films followed by heat treatment is one way that silicon is doped during the production of n-type or p-type semiconductors (Chapter 8). Following evaporation of a p-type or an n-type dopant onto a pure silicon substrate, the sample is heated to allow the dopant to diffuse into the silicon.

Chemical Vapor Deposition (CVD) and Molecular Beam Epitaxy (MBE)

One of the most popular techniques for achieving atomic-scale synthetic control is chemical vapor deposition (CVD). In this method, precursor gas molecules are thermally decomposed to yield solids of interest. With appropriate control, solids can be deposited virtually an atomic layer at a time onto a substrate.

Diamond provides an important illustration of the CVD methodology, which can be used to produce thermodynamically metastable products. As noted in Chapters 1, 7, and 9, diamond has many unusual and desirable physical and chemical properties but, until recently, had resisted all but brute force synthetic techniques that relied on extremely high temperatures and pressures. In the early 1980s, however, CVD methods were successfully brought to bear on the problem. In particular, gaseous mixtures of hydrogen containing a small amount of hydrocarbon gas (on the order of 1% methane, for example) were found to yield diamond films under conditions that led to the cracking of the hydrocarbon. Atomic hydrogen appears to play a crucial role in favoring diamond formation. In these low-pressure processes, atomic hydrogen is generated by various techniques, including microwave irradiation, flames, and use of a hot filament *(4)*.

The growth of semiconductors is routinely carried out by CVD methods. Commonly, reactive metal alkyls and nonmetal hydrides are co-reacted by thermally decomposing them onto a heated substrate. For example, equation 12 shows that trimethylgallium and arsine react to produce GaAs and methane:

$$(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3\ CH_4(g) \qquad (12)$$

To make a solid solution of $Al_xGa_{1-x}As$, a third precursor like $(CH_3)_3Al$ would be present as well:

$$x\ (CH_3)_3Al(g) + (1-x)\ (CH_3)_3Ga(g) + AsH_3(g) \rightarrow Al_xGa_{1-x}As(s) + 3\ CH_4(g) \qquad (13)$$

This technique permits the growth of atomically abrupt interfaces and thus of countless tailored solid structures. A solid formed, for example, by growing in repeated alternation 10 atomic layers of GaAs followed by 10 atomic layers of $Al_{0.1}Ga_{0.9}As$, has physically distinct properties from one grown by alternating five layers of each of these compositions. When the dimensions of the tailored features are sufficiently small, quantum size effects can be observed.

The nature of the interfaces formed between dissimilar materials is also important. Because of the chemical similarity of Al and Ga, the unit cell sizes of GaAs and $Al_xGa_{1-x}As$ (both have the zinc blende structure, Chapters 5 and 7, and cubic unit cell lengths of 5.66 Å) are almost identical, meaning that the deposited atomic layers are in near-perfect registry with one another, even when the composition switches from GaAs to $Al_xGa_{1-x}As$ or vice-versa. This kind of growth, wherein the atoms of the deposited layer are in registry with those beneath on the substrate, is called epitaxial growth. Mismatches that occur when there is more structural disparity between the deposited material and the substrate can lead to large concentrations of defects that may degrade the performance of devices constructed from these materials.

The p–n junctions described in Chapter 8 benefit greatly from CVD technology. Samples of GaAs can be grown by CVD in the presence of additional precursor gas molecules that serve as dopant sources. For instance, n-GaAs would result if hydrogen selenide were present during the growth. After a desired thickness of n-GaAs had been deposited, the dopant source could be switched to dimethylzinc to produce the p-type layer atop the n-type substrate and thus a sharp p–n junction (Chapter 8).

A second technologically important method of semiconductor growth that can afford even better control is molecular beam epitaxy, MBE. In this ultrahigh-vacuum deposition process, collimated beams of atoms or molecules impinge on a heated substrate. For example, Ga, As, and Al are heated in separate furnaces that are equipped with shutters, and the heated beams strike a suitable substrate. Like CVD, the MBE process permits the construction of layered structures with atomic-scale control.

Optical Fibers

Optical fibers are prepared using gas-phase techniques and represent an enabling technology that is being used to an ever greater extent to transmit information. In many cases these fibers are replacing metal wire, owing to the much greater density of information that can be carried: light can be modulated at higher frequencies than electrical current. The synthesis and processing of these materials blends several themes of importance to materials chemistry.

In its simplest form, an optical fiber consists of a core of an amorphous material (usually silica, SiO_2, glass) surrounded by another material called the cladding. The amorphous glass is a structure without the long-range, periodically repeating arrangements of atoms that characterize the crystalline solids discussed throughout much of this book. The critical property of the materials composing the optical fiber are the speed of light in the two media, which is c/n, where c is the speed of light in vacuum (3×10^{10} cm/s) and n is the refractive index of the material. When the core of the optical fiber has a larger refractive index than the surrounding cladding, total internal reflection results, meaning that the light is largely confined to the core and can be transmitted along the fiber with relatively little “leakage,” as shown in Figure 10.6.

Fibers may have either an abrupt or a gradual change in refractive index. Those in which the change is abrupt are called single-mode fibers and are designed to carry a single wavelength of light, and those with a graded index are called multimode and may carry more than one wavelength. A standard graded index optical fiber has a core diameter of 50–62.5 µm and a cladding diameter of 125 µm. Single-mode fibers have core diameters that are typically 8–9 µm with cladding diameters of 125 µm.

Laboratory. Experiment 15 describes a synthesis of silica.

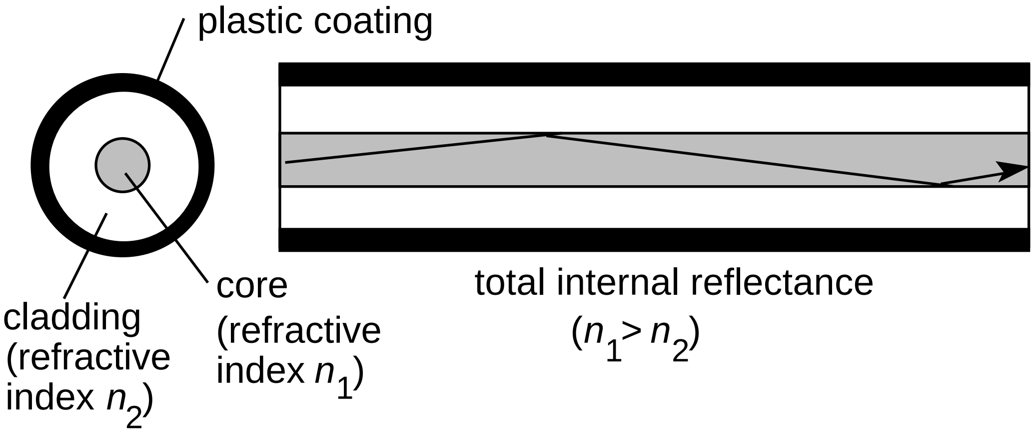


Figure 10.6. Cross-sectional (left) and longitudinal (right) views of an optical fiber. When the refractive index of the cladding is less than the refractive index of the core, light that is sent down the fiber core will tend to stay within the core.

Two materials-related limitations affect the efficiency of light transmission attainable in an optical fiber. First, scattering occurs because of defects in the glass. This so-called Rayleigh scattering increases as the wavelength of transmitted light decreases (it is proportional to λ^{-4}, where λ is the wavelength) so that relatively long wavelengths in the near-infrared are used. Wavelengths of 1300 and 1550 nm correspond to absorption windows (negligible absorption) in the silica core material and have been the focus of development efforts; these are also wavelengths that are accessible to the output of diode lasers corresponding to $In_xGa_{1-x}As_yP_{1-y}$ semiconductor solid solutions (Chapters 3 and 7). A second transmission loss mechanism involves transition metal impurities in the core material, which give rise to metal–oxygen vibrations that absorb over a broad spectral range. Thus, the glass must be very pure. In addition, the glass must be dry, because O–H bonds give rise to overtone bands that appear in the spectral region of interest.

Two general synthetic methods that minimize these problems have been developed for optical fibers. AT&T Bell Laboratories has developed a technique called the MCVD or modified chemical vapor deposition process. In MCVD, high purity $SiCl_4$ and O_2 ,which react to form SiO_2 and Cl_2, are passed through a fused silica (SiO_2) tube. In the first step, a high-purity cladding is deposited on the inside of the tube by passing a mixture of $SiCl_4$, O_2, and a fluorine-containing gas such as CCl_2F_2 or SiF_4 into the tube; the fluorinated gases supply fluorine, which lowers the refractive index of the silica. In the second step, the core material is passed into the tube. Small amounts of $GeCl_4$ (which reacts with oxygen to produce GeO_2) can be added to the $SiCl_4$ as a dopant to increase the refractive index of the core. By carefully monitoring and varying the concentration of reactant gases, the refractive index can be changed abruptly or gradually from the center to the outside of the fiber. The tube is simultaneously heated to high temperatures to fuse the deposited material into a uniform glass. Then the rod is drawn into a fiber and coated with a plastic to increase durability. These processes are shown in Figure 10.7A.

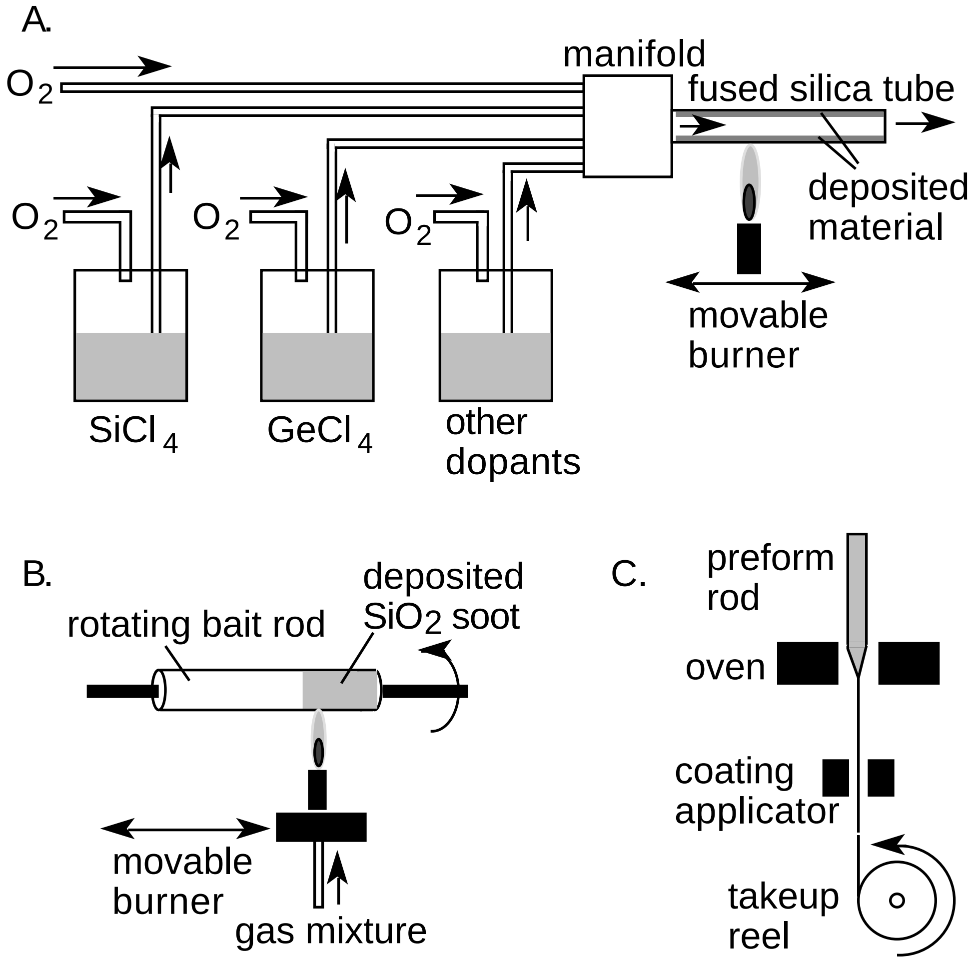


Figure 10.7. A: A schematic diagram of the MCVD process for preparing optical fibers. In this case material is deposited on the inside of a fused silica tube. (Adapted with permission from reference 5.) B: A schematic diagram of the OVD process. In this method, material is deposited on the outside of a bait rod, which is removed prior to pulling the fiber. C: A simplified diagram for the generation of a glass fiber from a preform rod generated by either method of preparation. (Adapted with permission from reference 6.)

Corning Glassworks has developed an alternative process called OVD, or outside vapor deposition, which involves depositing SiO_2 or Ge-doped SiO_2 on the outside of an alumina rod. In this case, $SiCl_4$ and other dopant gases such as $GeCl_4$ are fed into a flame to produce a soot of SiO_2 on a rotating alumina rod called a bait rod. By varying the composition of the gases in the flame, the refractive index of the deposited glass can be varied to create the core and then the cladding. After deposition, the bait rod is removed and the so-called soot blank, the material deposited on the alumina rod, is dried and heated to about 1600 °C to consolidate it into clear glass. Finally, it is drawn into a thin fiber and coated. This process is shown in Figure 10.7B.

Information is transmitted through the fiber by light from a laser or light-emitting diode (LED). The intensity of this light can be changed (turned on and off to correspond to logical 1s and 0s) to carry the digitized information. Many thousands of phone conversations can be carried on one optical fiber simultaneously through time-division multiplexing. In this technique, one second is divided into many segments, and each segment can be considered to be a channel for a separate conversation. If the transmitter and receiver are clocked and coupled, the conversations occur in separate time slots.

Chemie Douce or Soft Chemistry

Soft chemistry (or, in French, *chemie douce*) involves modifying an existing compound under relatively mild conditions to produce a closely related material. In an intercalation reaction, the basic structure of the host is not altered when a guest molecule is inserted. With reference to Figure 10.8, these can include the following reactions of guest molecules, $\bigcirc$ and $\boxed{+}$, with host solids, $\boxed{\quad\text{Host}\quad}$.

redox

$$n\bigcirc + \boxed{\text{Host}} \rightarrow \boxed{\oplus_n(\text{Host}^{n-})} \tag{14}$$

(where $\bigcirc$ is H^+ (and a reductant), Li, or Na)

ion exchange

$$n\boxed{+} + \boxed{\oplus_n(\text{Host}^{n-})} \rightarrow n\oplus + \boxed{\boxed{+}_n(\text{Host}^{n-})} \tag{15}$$

(where $\boxed{+}$ is H^+ or alkali and transition metal ions)

acid–base

$$n\bigcirc + \boxed{\text{H-Host}} \rightarrow \boxed{\text{H}\oplus_n(\text{Host}^{n-})} \tag{16}$$

(where $\bigcirc$ is an amine and H-Host has acidic protons available)

Because the reactions are generally run at relatively low temperatures, compounds and/or phases that are either metastable or not stable at elevated temperatures can be prepared.

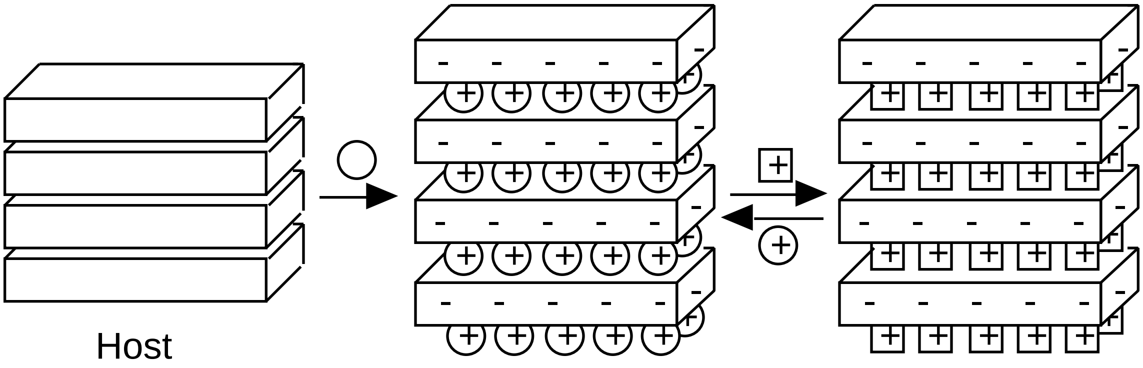


Figure 10.8. Chemical reactions of a layered material such as clays, graphite, MS_2 (M is a transition metal; MoS_2, for example), MOCl (FeOCl, for example), MPX_3 (M is a transition metal and X is S or Se; $CdPS_3$, for example), MO_x (MoO_3, for example), and $M(HPO_4)_2{\cdot}xH_2O$ (M is Ti, Zr, Hf, Ge, Sn, or Pb). The large blocks represent layers of the host material which have negative charge when positively charged guests are present.

Compounds such as β-alumina (approximately $Na_2O{\cdot}8Al_2O_3$) that have mobile ions can undergo ion exchange. The sodium ion in β-alumina can be replaced by a variety of monovalent cations such as Li^+, K^+, Ag^+, Cu^+, Tl^+, and NH_4^+ by immersing the compound in an appropriate molten salt at about 300 °C.

$$Na_2O{\cdot}8Al_2O_3(s) + 2\ AgNO_3(l) \rightarrow Ag_2O{\cdot}8Al_2O_3(s) + 2\ NaNO_3(l) \quad (17)$$

Zeolites readily undergo ion exchange of the compensating cation in the channel (for example, the Na^+ ion in $[Na_x(AlO_2)_x(SiO_2)_y]$). This ion exchange is used to soften water (to replace Mg^{2+}, Ca^{2+}, and Fe^{3+} in water with Na^+ by ion exchange) and to prepare catalytically active transition metal and lanthanide derivatives of zeolites.

Oxidation or reduction may accompany loss or gain of an ion. In Experiment 8, the reaction of HCl with zinc metal generates hydrogen atoms, which can intercalate into the cavities in the structure of WO_3. The product of this reaction is H_xWO_3, which is highly colored and conducting due to the donation of electrons from the hydrogen atoms into the conduction band of the WO_3. H_xWO_3 is used in sunglasses and automobile rear-view mirrors.

$$x\ HCl(aq) + x/2\ Zn(s) + WO_3(s) \rightarrow H_xWO_3(s) + x/2\ ZnCl_2(aq) \quad (18)$$

Host solids with acidic protons, such as $Zr(O_3P\text{-}OH)_2{\cdot}H_2O$, have been shown to undergo reactions with bases (Figure 10.9).

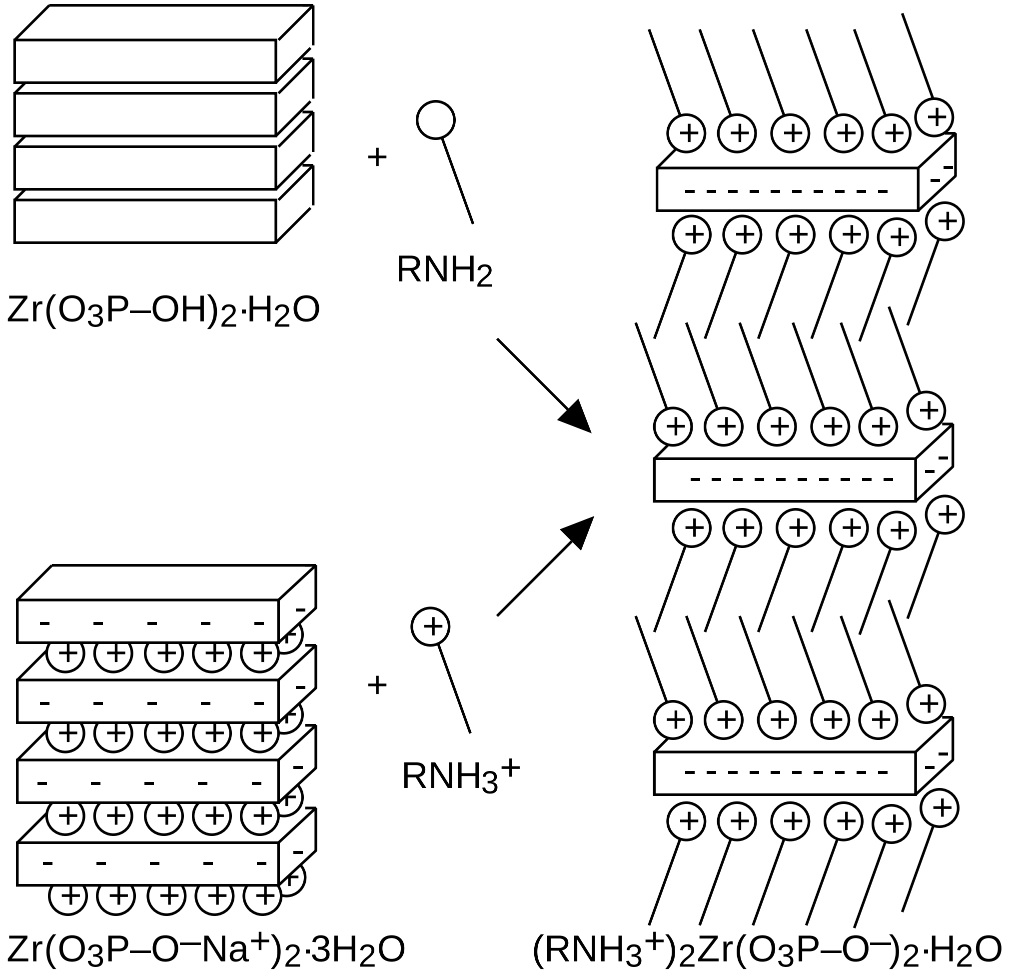


Figure 10.9. Two ways to produce an alkyl ammonium-intercalated zirconium phosphate layered solid. The top reaction shows zirconium hydrogen phosphate reacting with an alkyl amine, RNH_2, in an acid–base reaction. The bottom reaction shows zirconium sodium phosphate reacting with an alkyl ammonium ion, RNH_3^+, in an ion-exchange reaction that releases sodium ions to the solution.

Preparation of Large, Pure Crystals

Workers in processing areas at electronics companies often dress in white coveralls, gloves, cloth boots, caps, and face masks. The protective clothing is not needed to protect the workers: it is used to keep the components clean. As noted in Chapter 8, control of chemical composition at the parts-per-million level (and below) is critical for many electronic applications of solid materials. The electronic applications of microcircuits would be impossible were it not possible to prepare pure samples of silicon as large single crystals.

Zone Refining

Zone refining is a technique for purifying a solid that takes advantage of the fact that as a solution freezes, crystals of the pure solvent are formed. When part of a sample of ocean water freezes, the ice that forms does not contain appreciable concentrations of salt; the salt remains in the liquid water.

Zone refining occurs when a long sample is slowly drawn through a temperature gradient (a change in temperature that occurs over a particular distance) that is sufficiently narrow that only a small section of the sample is melted at any point. Figure 10.10 illustrates one arrangement of sample and furnace. As the sample enters the furnace from the left, the sample at the right end of the container melts first, and impurity phases dissolve in the melt. As the container continues to move through the furnace, the right end of the melt leaves the hot zone and freezes. Because the impurities remain in the melt, the crystal that results is purer than the initial sample. As the sample is drawn through the furnace, the molten zone with its impurities moves toward the left end of the sample. Ultimately, the impurities have been concentrated in the left side of the sample and can be cut off and discarded. Very pure samples can be produced by repeating the process several times, provided the molten sample does not react and pick up impurities from the container or from the atmosphere.

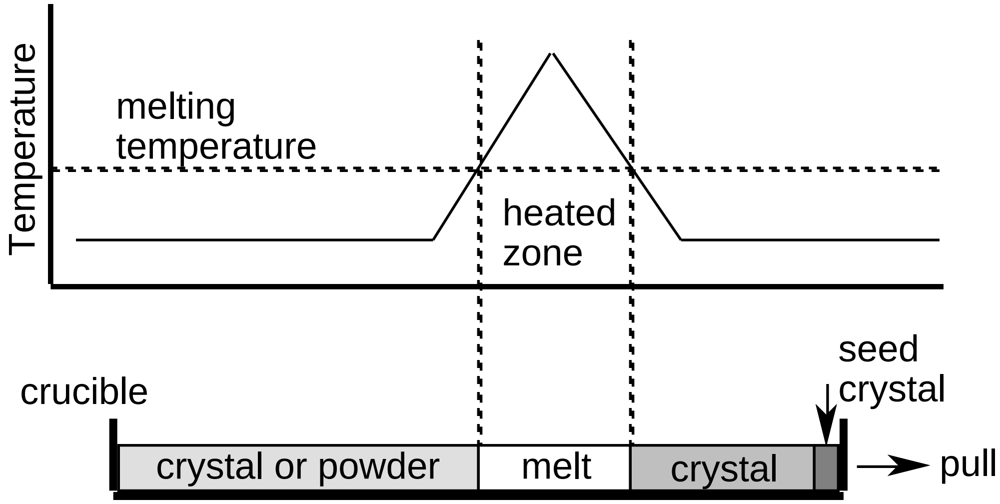


Figure 10.10. A schematic of the zone-refining process. The melting temperature of the pure sample is shown by the horizontal dashed line. (Adapted with permission from reference 2.)

Czochralski Crystal Growth

Large cylinders of single-crystal silicon and other single crystals are produced by the Czochralski process (Figure 10.11). In some ways this process is reminiscent of zone refinement: A crystal forms as a melt passes through a temperature gradient from a hot zone to a cooler zone, and impurities remain in the melt. In this case, however, the sample starts out molten.

To start crystal growth, a seed crystal is placed in contact with the surface of a melt in a furnace with a temperature only slightly above the melting point of the sample. As the seed is pulled from the melt, the melt adheres to the crystal and is pulled into the cooler region of the furnace. It solidifies on the seed and the solidified portion continues to move liquid from the melt into the cooler portion of the furnace. The melt and growing crystal are usually rotated in opposite directions during pulling to maintain a constant temperature and uniform melt. A very pure inert gas is used to provide a nonreactive atmosphere for the process.

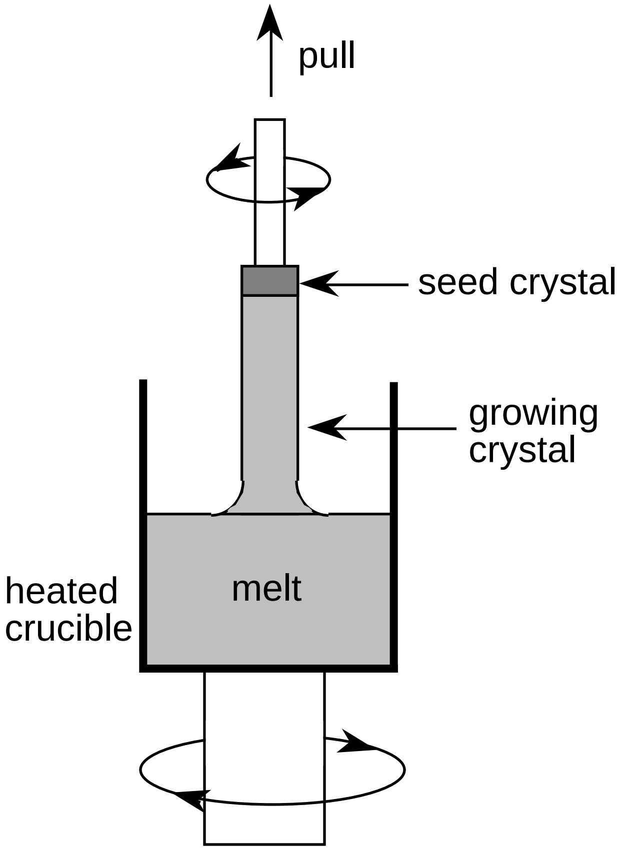


Figure 10.11. Czochralski method for crystal growth. (Adapted with permission from reference 2.)

This method is widely used for growing large single crystals of Si, Ge, GaAs, and other semiconductors. Thin silicon disks (wafers) used to make microelectronic chips are sawed from silicon crystals that can be several inches in diameter and several feet long.

References

1. Shakhashiri, B. Z. *Chemical Demonstrations: A Source Book for Teachers*; University of Wisconsin Press: Madison, WI; Vol. 1, 1983; pp 85–89.
2. West, A. R. *Solid State Chemistry and Its Applications*; John Wiley and Sons: New York, 1984; pp 19–36.
3. Brennan, J. G.; Siegrist, T.; Stuczynski, S. M.; Steigerwald, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 9240–9241.
4. Wold, A.; Dwight, K. *Solid State Chemistry*; Chapman & Hall: New York, 1993; pp 201–202.
5. *Optical Fiber Communications; Volume 1. Fiber Fabrication*; Li, T., Ed.; Academic Press: Orlando, FL, 1985; p 3.
6. Keiser, G. *Optical Fiber Communications*; McGraw-Hill: New York, 1983; p 277.

Additional Reading

- Cheetham, A. K.; Day, P. *Solid State Chemistry: Techniques*; Clarendon Press: Oxford, England, 1987, Chapter 1.
- West, A. R. *Solid State Chemistry and Its Applications*; John Wiley and Sons: New York, 1984; Chapter 2.
- *Intercalation Chemistry*; Whittingham, M. S.; Jacobson, A. J., Eds.; Academic Press: New York, 1982.
- Wold, A.; Dwight, K. *Solid State Chemistry*; Chapman & Hall: New York, 1993; Chapter 6.

Acknowledgments

We thank Scott Shenk, Paul Lemaire, and Jim Flemming of AT&T Bell Laboratories; Scott Slavin of Rohm and Haas; John Geisz, University of Wisconsin—Madison, Department of Chemical Engineering; John Perepezko, and Jim Foley, University of Wisconsin—Madison, Department of Materials Science and Engineering; Mark Thompson, Princeton University, Department of Chemistry; and John Smith, University of Wisconsin—Madison, Communications Service Manager for their help.

Exercises

1. Explain why adding solid lead nitrate to solid potassium iodide at room temperature gives a very low yield of lead iodide, but adding a solution of lead nitrate to a solution of potassium iodide gives essentially a 100% yield of lead iodide.

2. How could the yield of lead iodide from the reaction of solid lead nitrate and solid potassium iodide be increased under anhydrous conditions (without adding water)?

3. Explain why heating Co with Co_3O_4 in air cannot be used to prepare CoO.

4. Write balanced equations for the following syntheses.
   a. $TiVO_4$ from Ti_2O_3 and V_2O_5
   b. $PbNbO_3$ from Pb, PbO, and Nb_2O_5
   c. TiS_2 from Ti and S
   d. $CrCl_2$ from reduction of solid $CrCl_3$ with H_2
   e. MnO from solutions of $MnCl_2$ and NaOH (two steps)
   f. The product resulting from adding $SiCl_4$ to water followed by heating the solid produced in air.

5. Suggest an explanation for why LiI reacts with V_2O_5 to produce $Li_xV_2O_5$ but LiCl will not react.

6. Suggest an explanation for why LiI reacts with V_2O_5 to produce $Li_xV_2O_5$, but CsI will not react.

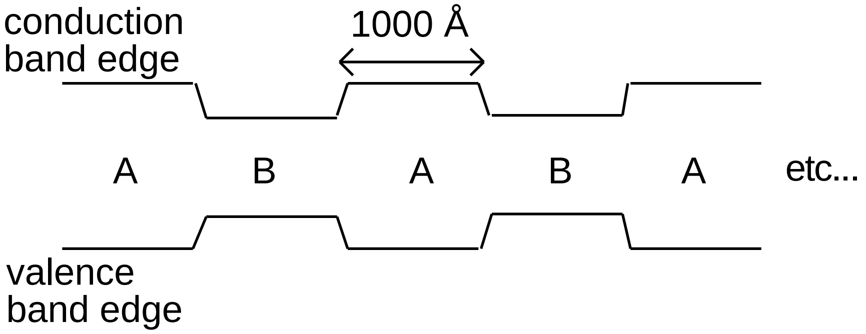
7. $LaFeO_3$ can be prepared by heating (in air) a mixture of $La_2(CO_3)_3$ and Fe_2O_3 at 1200 °C for 24 hours, grinding the product, and repeating the heating for an additional 24 hours. Alternatively, $LaFeO_3$ can be prepared by heating (in air) the La^{3+} salt of the $Fe(C_2O_4)_3^{3-}$ ion for 8 hours at 1000 °C. Explain why one requires more vigorous reaction conditions.

8. Consider three solids: an equimolar physical mixture of AlAs and GaAs, a $Al_{0.5}Ga_{0.5}As$ solid solution; and a solid consisting of equal total numbers of AlAs and GaAs layers where, using CVD methods, 10 layers of each composition had been deposited at a time. Qualitatively compare these three solids with regard to elemental analyses and their X-ray diffraction patterns.

9. Sketch five different structures in cross section that could be grown by CVD that would analyze as having 1:1 A:Z composition (chemical formula AZ). How would you physically distinguish them?

10. In the spinel ($MgAl_2O_4$) structure mentioned in this chapter, it was noted that the oxide ions were in a ccp arrangement, the Mg^{2+} ions were in tetrahedral holes, and the Al^{3+} ions were in octahedral holes. What fraction of the tetrahedral holes are occupied? What fraction of the octahedral holes are occupied?

11. A structure containing alternating 1000-Å-thick layers of GaAs (E_g = 1.4 eV) and $Al_{0.3}Ga_{0.7}As$ (E_g = 1.9 eV) has the idealized electronic structure:



a. Which of the two compositions corresponds to the regions labeled A and which to those labeled B?
b. To which region (A or B) will conduction band electrons go to reach lower energy? To which region (A or B) will valence bond holes go to reach lower energy?
c. In which regions (A, B, both or neither) will the following photon energies be absorbed?
   - i. 1.6 eV
   - ii. 1.1 eV
   - iii. 2.5 eV

12. Sketch part of the structure of the amorphous silica used in optical fibers showing how germanium atoms might be incorporated into the structure as a dopant. How might fluorine atoms be incorporated into the structure?

13. The value of the heat of formation, ΔH_f^o, for $Ni_{0.5}Al_{0.5}$ has been estimated to be –59,000 J/g.
    a. To what reaction does this correspond?
    b. If the specific heat capacity of this alloy is about 25 J/g-^{o}C, estimate the temperature reached during this reaction.

14. Use unit-cell lengths in Appendix 5.6 to suggest combinations of metals that could be grown epitaxially on one another.

15. Explain why ZnSe can be grown epitaxially on GaAs. What other semiconductor combinations might be expected to be amenable to epitaxial growth?