29

Growing Single Crystals

CHAPTER PREVIEW

We will now describe the important methods used to produce single crystals of ceramic materials. Single crystals are important in many applications ranging from synthetic gemstones for jewelry to hosts for solid-state lasers. The method that is selected to grow a particular type of crystal depends on several factors. The selection criteria are determined by the properties of the material—whether a suitable solvent can be found, if the solid melts congruently or incongruently, or if it sublimes, and the economic factors—the volume of material to be produced and the capital equipment costs. Remember that without the growth of ceramic single crystals, the Si Age would never have happened.

29.1 WHY SINGLE CRYSTALS?

For some applications, ceramic materials must be prepared as single crystals. When used as substrates for thin-film growth [e.g., silicon-on-sapphire (SOS) technology or the growth of superconductor thin films] it is the crystalline perfection of a single crystal that is important. In optical applications, e.g., the use of ruby and yttrium–aluminum–garnet (YAG) for laser hosts and quartz and sapphire for optical windows, single crystals are used to minimize scattering or absorption of energy. In piezoelectric materials, e.g., quartz, the optimum properties are obtained in single-domain single crystals. Table 29.1 lists some of the applications that utilize the desirable optical, electrical, magnetic, or mechanical properties of ceramic single crystals.

Because preparing single crystals is in most cases a more difficult and expensive process than preparing the same compositions in polycrystalline form they are often much more expensive than their polycrystalline counterparts. For example, you can buy 99.9% pure MgO powder in small quantities for about $2/gram. Single crystal slices of MgO of the same purity cost about $300/gram! The increased cost of the single crystal not only involves the extra processing costs but may also include costs associated with orienting, cutting, and polishing.

When used for jewelry, synthetic single crystals can be more costly than naturally occurring ones. For example, the cost of a gem-grade faceted synthetic diamond may be 10 times that of an equivalent natural diamond. However, flux-grown emeralds and rubies are about one-tenth the cost of natural stones of comparable quality. (The synthetic stones are often much more perfect than the natural ones.) Large single crystals of cubic ZrO_2, which are used as diamond simulants, are available only as synthetics. In its pure form the cubic polymorph of zirconia is not stable at room temperature and must be stabilized by the addition of CaO, MgO, or Y_2O_3. The cubic form of ZrO_2 does exist in nature; it was discovered in 1937 as tiny crystals in an amorphized piece of zircon ($ZrSiO_4$), but it is not abundant.

29.2 A BRIEF HISTORY OF GROWING CERAMIC SINGLE CRYSTALS

Although crystal growth is a relatively new industry, we can trace its origin back to 2500 BCE when salt was purified by crystallization. Systematic work in crystal growth started in c. 1600 CE with the growth of crystals from aqueous solution and in c. 1850 from the melt and the vapor.

Hydrothermal growth. Growth of large single crystals of a ceramic material using the hydrothermal growth method was first demonstrated for α-quartz. This method uses an aqueous solution that is usually heated and pressurized. The growth process closely reproduces the growth of amethyst in nature. The principle is essentially the same as used for growing salt or copper sulfate crystals in high school. Silica is soluble in water, which is where diatoms find their silica. The special feature of the hydrothermal growth of quartz is the use of pressure to increase the solubility of SiO_2 in H_2O.

Flux growth. First practiced by French and German chemists and mineralogists in the late 1800s, this technique is also known as molten-salt growth. Flux growth did not become an important method for forming single crystals until the 1950s. A particularly significant

TABLE 29.1 The Uses of Single Crystals

Semiconductor devices	
1. Diodes	Si, Ge
2. Photodiodes	Si, GaAs, $Cd_xHg_{1-x}Te$
3. Transistors	Si, GaAs, SiC
4. Thyristors	Si
5. Photoconductive devices	Si, $Cd_xHg_{1-x}Te$
6. Integrated circuits	Si, GaAs
7. Light-emitting diodes	GaAs, GaN, SiC
8. Radiation detectors	Si, Ge, CdTe, YAG
9. Strain gauges	Si
10. Hall effect magnetometers	InSb
Mechanical components	
1. Abrasives and cutting tools	SiC, Al_2O_3
2. Substrates	Diamond, Al_2O_3
Magnetic devices	
1. Transformer cores	Ferrites
2. Electric motors	Ferrites
3. Tape heads	Ferrites
4. Microwave circulators	Garnets
Piezoelectric devices	
1. Resonant bulk wave devices	SiO_2, $LiTaO_3$
2. Surface wave devices	SiO_2, $LiNbO_3$, AlN
Optical devices	
1. Windows	Al_2O_3
2. Lenses	CaF_2
3. Polarizers	$CaCO_3$
4. Laser hosts	YAG, Al_2O_3, alexandrite
5. Magnetooptical devices	YIG
6. Electrooptic devices	$LiNbO_3$, ADP, KDP
7. Nonlinear devices	ADP, KDP, $LiNbO_3$
Jewelry	Diamond, cubic zirconia
Pyroelectric devices	
X-ray and particle optical devices	
1. Collimators and focusing elements	SiO_2

contribution during this time was the growth of $BaTiO_3$ single crystals using a KF flux at Bell Telephone Laboratories in New Jersey. These crystals were of interest to Bell Labs for ferroelectric storage elements for digital computers and telephone switching systems. Single crystals were preferred over polycrystalline sintered $BaTiO_3$ ceramics because the single crystals had a more rectangular hysteresis loop and lower coercive fields. (See Chapter 31 for more on ferroelectric ceramics.)

Verneuil, Czochralski, and Bridgman. The Verneuil process, also known as the flame-fusion method, was first described in 1902 by Auguste Verneuil. His original apparatus has been preserved and is in the Museum of Arts and Sciences (Musée des Arts et Métiers) in Paris. This process was used in the early 1900s to make synthetic rubies. Although the initial application for these crystals was in jewelry, their hardness made them suitable for bearings in clocks and watches, which eventually has become their main use. Other methods for growing crystals from the melt followed. Pulling the crystal from the melt was first practiced by Czochralski (Cz) in 1917. He grew crystals of low-melting temperature metals including Sn, Pb, and Zn. Single crystals of Ge and Si were first produced by the Cz method in 1950. This process is now used in the semiconductor industry for preparing very large single crystals of Si and, with some slight modifications, it can be used to produce single crystals of compound semiconductors (e.g., GaAs). The first oxide crystals to be grown extensively by the Cz process were calcium tungstate ($CaWO_4$), a laser host. Melt growth of single crystals in crucibles was first used by Bridgman and the method was significantly improved by Stockbarger and became known as the Bridgman–Stockbarger method.

Two melt-growth techniques that have emerged since 1950 are zone refining and the floating-zone (FZ) method; some of the thin-film methods discussed in Chapter 28 can also be thought of as melt techniques. Zone refining is used to purify single crystals (also for polycrystals). Although zone refining is applicable to all types of single crystal, its use is widespread only in the semiconductor industry where crystal purity is of great concern. The FZ method was first applied to the growth of Si crystals. It has since been used to form single crystals of other ceramics but is mainly limited to high-purity Si.

Although vapor-phase techniques are widely used to make thin films they are not used extensively in the growth of large single crystals. One of the most interesting vapor-phase methods is the vapor–liquid–solid (VLS) mechanism first identified by Wagner and Ellis. This mechanism allows the growth of thin single-crystal whiskers that can be used as reinforcements in ceramic-matrix composites (see Chapter 20). It is also widely discussed regarding the growth of nanotubes, nanowires, and nanosprings.

29.3 METHODS FOR GROWING SINGLE CRYSTALS OF CERAMICS

The growth of single crystals involves one of the following changes of state:

- Liquid (pure or solution) → solid
- Gas → solid

The atomic or molecular species in a fluid are, on average, arranged randomly. During crystal growth they must move to the correct sites in the ordered structure of the crystalline phase. If crystal growth is too rapid, disordered regions (crystal lattice defects such as dislocations) are trapped in the crystal or many smaller crystals with varying orientations are nucleated thereby destroying the desired single-crystal perfection. The growth process involved in producing a single crystal must therefore be slow and so it requires precise control over the growth conditions (e.g., temperature) for prolonged periods.

Several different methods are used commercially to grow single crystals. These methods, which can be divided into melt, solution, and vapor-phase techniques, are summarized in Table 29.2. Here, the operating cost does not include the cost of labor, the skill refers only to the diffi-

TABLE 29.2 Factors Relevant to the Choice of a Growth Technique for Crystal Production

	Equipment investment	*Operating costs*	*Skill needed*	*Development needed*	*Range of materials*	*Growth rate*	*Crystal perfection*
Cz	High	Medium	Medium	Medium	Many	Rapid	High
Bridgman	Low	Medium	Low	Little	Many	Medium	Medium
Verneuil	Medium	Low	High	Little	Some	Rapid	Low
Skull melting	High	Medium	Medium	Medium	Some	Rapid	Medium
Flux	Medium	Medium	Low	Much	Few	Slow	Variable
Hydrothermal	Very high	High	Medium	Much	Few	Slow	Variable
UHP	Very high	High	High	Much	Few	Slow	Variable
Gas phase	Low	Low	Low	Varies	Few	Very slow	Variable

culty in using the equipment, not in developing the process, the crystal perfection assumes the optimum conditions, not the fastest, and the rate of flux growth depends on the complexity of the reaction—as is the case with growth of emerald.

The method chosen depends on the type of crystal, the application for that crystal, and the required size. The most widely used growth technique is the Cz process because it can produce very large dislocation-free crystals of silicon. It is also used to form single crystals of many oxides. For oxides containing more than one cation the general requirement for forming a crystal by the Cz process is that the material melts congruently. In such cases crystal growth of compounds by pulling is similar to growing elemental crystals. If the compound melts incongruently the Cz method can still be used, if special precautions are taken, or an alternative method, e.g., growth from solution or from a flux, may have to be used.

Most methods of single-crystal growth seek to control the nucleation of the crystalline phase. This is achieved by arranging for the crystal to grow on a "seed" (which is the nucleus). The seed crystal is usually a single crystal of the same composition as the crystal to be grown. It is often oriented in such a way as to facilitate growth of one specific crystalline orientation. In the Bridgman–Stockbarger method a seed crystal is not used. In this method advantage is taken of the tendency for crystals to grow more rapidly in one crystallographic direction than in another.

SINGLE-CRYSTAL TERMINOLOGY

A large single crystal in the as-grown form is often referred to as a *boule*, from the French word for ball, or as an *ingot* (which may also be used to describe a polycrystal).

When a boule is cut into flat sections, the single-crystal slices are typically referred to as *wafers*.

When the wafers are cut into small units (usually either square, rectangular, or circular) they are referred to as *substrates* or *windows*.

Vapor-phase techniques are not as widely used as growth from the melt or solution because the growth rate is generally slow or only small crystals can be grown. However, two vapor-phase techniques have commercial application: the growth of whiskers or small islands (e.g., SiC and GaN) by the VLS process and the growth of SiC and nanotubes by sublimation processes.

Many other techniques can be used to produce single crystals; solid–solid phase transformations or growth from gels are modern examples. Although such methods may be useful in the laboratory for producing small single crystals of ceramics they are not currently of commercial importance.

29.4 MELT TECHNIQUE: VERNEUIL (FLAME-FUSION)

The Verneuil, or flame-fusion, method is illustrated in Figure 29.1. It is a well-established technique for growing single crystals of oxides that have high melting temperatures. The largest application of the Verneuil method is for the growth of sapphire and ruby.

For growing sapphire crystals, high-purity aluminum oxide powder of a uniform particle size is fed at a controlled rate down a tube at the end of which the particles are melted by an oxyhydrogen flame. The molten particle then falls into a shallow (~20-μm-deep) pool of liquid on top of a seed crystal. The pool of liquid is held on the seed crystal by surface tension. The seed is lowered into the annealing zone of the furnace at the same rate as the new material arrives, thus growing the crystal. The growing crystal cools slowly helping to reduce strains and minimizing the chance of forming lattice defects. It is always preferable to anneal the crystal from the growing temperature without first cooling to room temperature. If the crystal is first cooled to room temperature and then annealed it is much more difficult to remove any defects that have formed. Remember that the crystal will still contain point defects as these are equilibrium defects at high T and so cannot easily be annealed out. Since a gas flame and powder are used in the process, trapped pores are common defects.

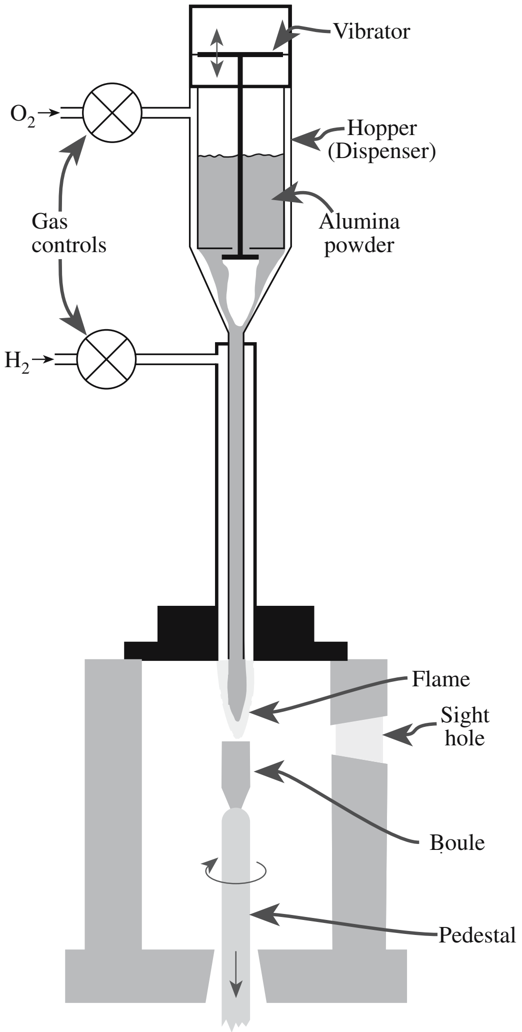


FIGURE 29.1 The Verneuil technique.

To produce artificial rubies and sapphires various transition metal oxides are added to the alumina feed powder. For rubies, between 1 and 3 at% Cr_2O_3 gives the characteristic deep red color. Artificial blue sapphires are obtained when a mixture of 1 at% TiO_2 and 2 at% FeO is added to the feed powder.

One advantage of the Verneuil method is that it does not use a crucible to contain the melt—only a shallow pool of liquid is present throughout the growth process. An important constraint of liquid-to-solid transitions for crystal growth is the reaction of the melt with the container. For crystals with a high melting temperature (the situation we often encounter in ceramics) this constraint becomes especially severe. Even if reactivity is not a problem it is still difficult to find suitable containers that can withstand very high temperatures without melting or degrading. The other advantages of the Verneuil method are that it is relatively inexpensive and quick. Crystals can easily be obtained in a matter of hours (typical growth rates are 10^{-2} m/h) compared with the months needed for some solution techniques.

The main disadvantage of the Verneuil process is that there is relatively poor control over the growth parameters, particularly the temperature, because of the very small melt volume. As a consequence the quality of the crystal is often inferior to that obtained by, for example, the Cz method. Typically, Verneuil-grown crystals have high dislocation densities, which makes them most suitable for applications in which such imperfections are not so important (e.g., jewelry or jewel bearings). Very large single crystals cannot be produced by the Verneuil method. Verneuil-grown boules may be up to 9 cm in diameter. Table 29.3 lists some of the ceramic crystals that have been grown by the Verneuil method. Verneuil sapphire is used as the starting material (crackle) for Cz sapphire.

The FZ method shares many similarities with the Verneuil method. The main difference is that the source is a dense polycrystalline rod of the same composition as the desired single crystal, rather than the free-flowing powder used in the Verneuil method, but it still uses a constrained volume of liquid. The advantage of

STALAGMITES

The Verneuil technique is related to the growth of stalagmites in nature. Liquid drips (from the stalactite) onto the stalagmite, but instead of settling there and freezing (like a stalagmite icicle would) some of the mineral content is deposited as the water evaporates.

TABLE 29.3 Crystals Grown by Verneuil and Arc-Image Techniques

Material		*Comments*	*T_M (°C)*
Al_2O_3	Corundum, sapphire	Growth in a variety of directions; best growth in a cone of directions 60° from *c*	2040
Al_2O_3: Cr	Ruby	Verneuil	
$MgAl_2O_4$	Magnesium-aluminum spinel	Verneuil	2130
$3Al_2O_3 \cdot 2SiO_2$	Mullite	Verneuil	1810
$CaWO_4$	Scheelite	Verneuil	1530
TiO_2	Rutile	Verneuil	1830
ZrO_2	Zirconia	Verneuil	2700
Y_2O_3	Yttria	Verneuil	2400
$MgFe_2O_4$	Magnesium (nonstoichiometric) spinel	Arc-image	>1200
$NiFe_2O_4$	Nickel ferrite	Arc-image	>1200

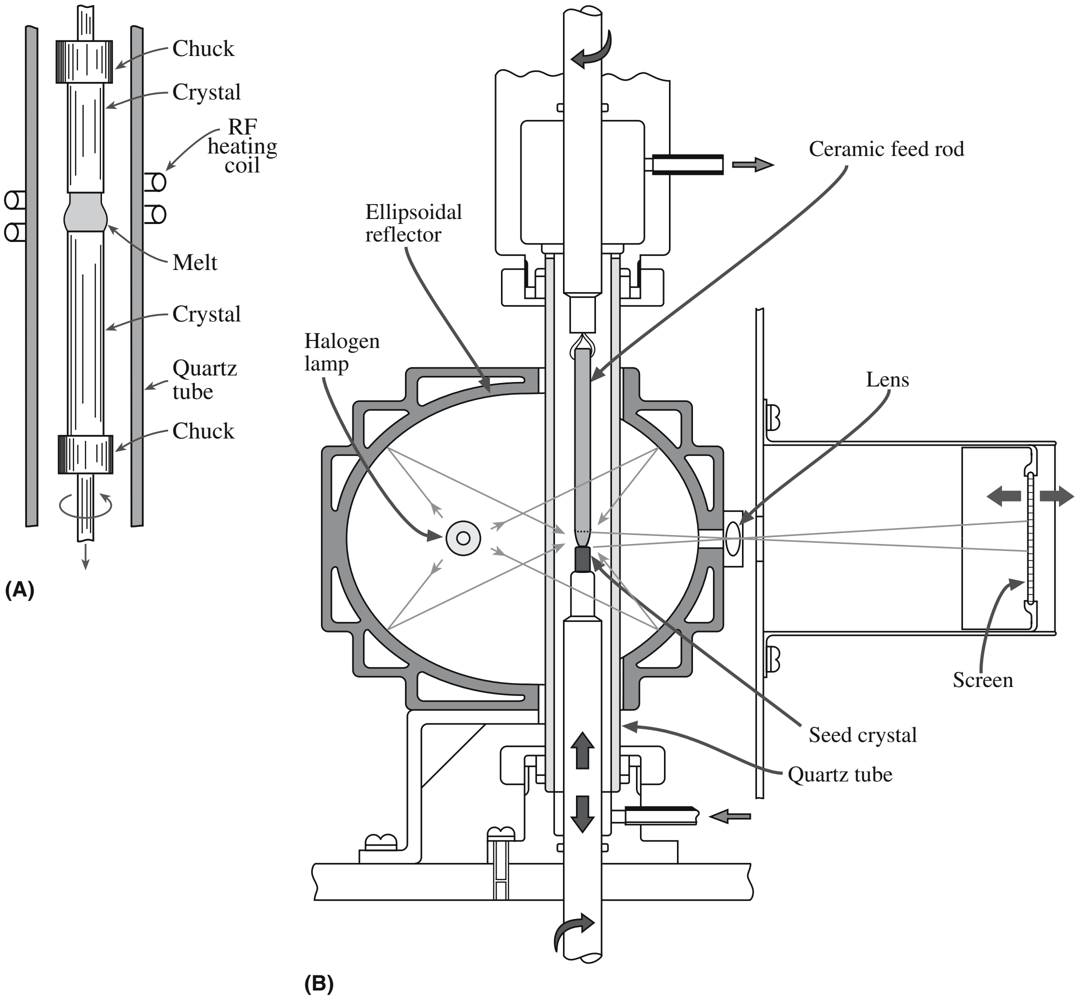


FIGURE 29.2 (a) Vertical float zone. (b) Arc image furnace.

the FZ method is that like the Verneuil method, no crucible is used: the material is its own crucible as shown in Figure 29.2a. A thin region of melt is again held in place by surface tension, this time between two parts of the feed rod. Not having a container removes one possible source of contamination; this is why the FZ method is used to produce high-resistivity silicon. The disadvantages of the FZ method are that it is not as amenable as the Cz method for producing very large high-quality single crystals. For ceramics the FZ method may use the arc-image heating method to attain the necessary high temperatures.

29.5 MELT TECHNIQUE: ARC-IMAGE GROWTH

Several techniques for growing single crystals combine aspects of the FZ method and the Verneuil flame fusion method, but the heat source is not a flame. One such "modified" FZ growth technique is called arc-image growth. Heat is supplied using a focused light source. Figure 29.2b shows a schematic arrangement of the arc-image growth process. The radiation from the light source is focused by parabolic reflectors and allows sample temperatures >2500°C to be attained. If a controlled or inert atmosphere is needed around the sample then it can be enclosed in a suitable transparent tube (envelope). $MgFe_2O_4$, and $NiFe_2O_4$, have both been grown by this technique. The main advantage of using arc-image heating is that it is easy to provide a clean high-temperature environment with a controllable atmosphere (which is particularly important when Fe cations are involved).

29.6 MELT TECHNIQUE: CZOCHRALSKI

A schematic diagram of the Cz technique is given in Figure 29.3a. The melt is kept at a temperature just above its freezing point and a seed crystal, rigidly fixed to a rotating tube, is lowered into the surface of the melt. The temperature of the melt is reduced until the molten material begins to freeze onto the seed. Pulling is then started and more material solidifies onto the crystal as it is withdrawn. The shape of the meniscus is determined by the

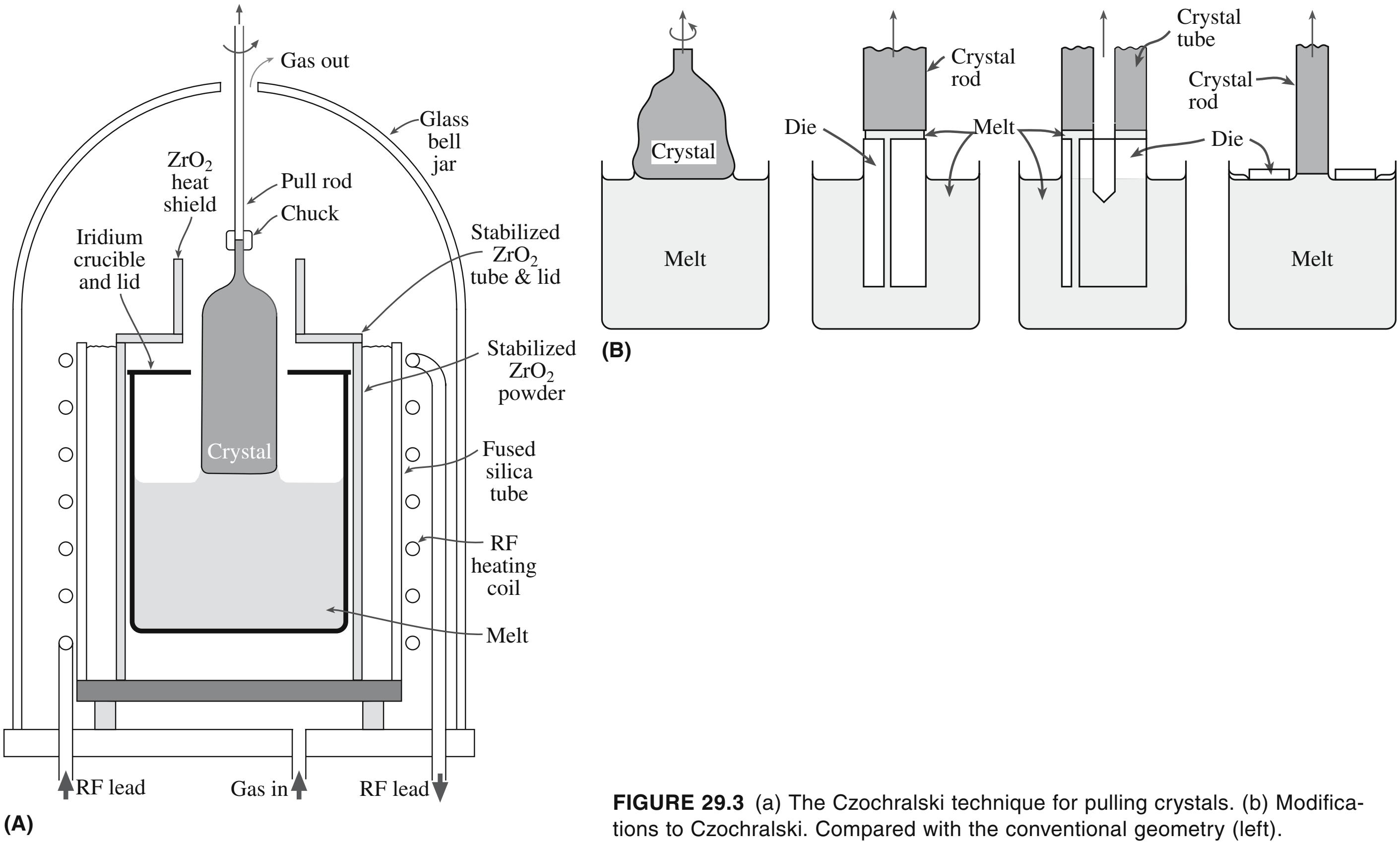


FIGURE 29.3 (a) The Czochralski technique for pulling crystals. (b) Modifications to Czochralski. Compared with the conventional geometry (left).

surface tension of the liquid. The seed crystal is normally rotated as it is withdrawn to average out any thermal asymmetries in the heating elements. This rotation also produces a stirring action, which can help homogenize the melt. At the same time, it accelerates crucible erosion and hence can introduce additional impurities into the melt. In cases in which the impurity concentration must be kept to a minimum the crucible containing the melt and the crystal can be rotated at the same rate and in the same direction! For nonoxide crystals the whole apparatus is maintained in an inert environment (e.g., Ar). Table 29.4 summarizes the relevant growth conditions that have been used to produce different crystals. A variation is to use a die to produce tubes, fibers, or sheets of sapphire or garnet as illustrated in Figure 29.3b. Actually single-crystal tubes can be produced inside single-crystal tubes.

TABLE 29.4 Materials Grown by the Cz Technique (for Crystals ~2 cm in Diameter)

Material	*T_M (°C)*	*Crucible*	*Atmosphere*	*Pulling rate (mm/h)*	*Rotation rate (rpm)*
Zn	419	Pyrex	Vacuum	400–800	10–30
GaSb	712	Graphite	Hydrogen	50–100	10–30
$FeGe_2$	866	Alumina	Vacuum	5–20	20–50
$Bi_{11}GeO_{20}$	930	Platinum	Oxygen	5–15	10–50
Ge	937	Graphite	H_2/N_2	60–120	20–50
$ZnWO_4$	1200	Platinum	Air	8–16	50–100
GaAs	1237	Silica	Arsenic	20–30	10–30
$LiNbO_3$	1250	Platinum	Oxygen	3–8	20–30
$Sr_xBa_{1-x}Nb_2O_6$	1400	Platinum	Oxygen	3–6	10–20
Si	1420	Silica	Argon	100–200	10–20
$MnFe_2O_4$	1500	Iridium		3–6	10–20
$CaWO_4$	1650	Rhodium	Air	8–16	50–100
$LiTaO_3$	1650	Iridium	Nitrogen	8–15	20–40
$Y_3Al_5O_{12}$	1950	Iridium	Nitrogen	1–3	40–60
Al_2O_3	2037	Iridium	Argon	1–3	30–50
$MgAl_2O_4$	2100	Iridium	Argon	4–8	20–40

FIGURE 29.4 Lower part of sapphire boule grown by the Cz technique, the boule was 100–150 mm diameter; 300 mm long.

Figure 29.4 shows part of a sapphire boule produced by the Cz process. Sapphire boules can be up to 150 mm in diameter and 600 mm in length and weigh >40 kg. Most sapphire is grown in the *r*-plane orientation (the growth axis is normal to the *r* plane). If an Si crystal is grown with a 300 mm (12 inches) diameter to a length of 0.5 m, the crystal weighs ~82 kg.

To determine the factors that affect the growth rate of the crystal we need to consider the heat flow in the system. The heat input, q_{in}, to the crystal across the crystal/melt interface is given by the sum of the heat associated with crystallization, q_{L}, and the heat flow from the melt, q_{M}:

$$q_{\text{in}} = q_{\text{L}} + q_{\text{M}} \tag{29.1}$$

q_{L} is given by

$$q_L = A\rho_s \Delta H_{\text{fus}} \frac{dx}{dt} \tag{29.2}$$

where *A* can be considered to be the area of the crystal at the liquid–solid interface. Actually, *A* is the area of the isotherm that goes through a point in the liquid close to the interface; however, very close to the interface this area is approximately the liquid–solid interfacial area. The density of the solid is ρ_s, ΔH_{fus} is the heat of crystallization (fusion), and *dx/dt* is the rate of growth. To a good approximation the growth rate can be considered equal to the pulling rate, which from Eq. 29.2 we can see is inversely proportional to *A*. Therefore the faster the crystal grows, the smaller its diameter.

The heat flow from the melt, q_{M}, is given by

$$q_M = Ak_{\text{L}} \frac{dT}{dx_{\text{L}}} \tag{29.3}$$

where k_{L} is the thermal conductivity of the liquid and dT/dx_{L} is the thermal gradient in the liquid. q_{in} is also the heat flow down the crystal, which is given by

$$q_{\text{in}} = Ak_{\text{s}} \frac{dT}{dx_{\text{s}}} \tag{29.4}$$

where k_{s} is the thermal conductivity of the crystal and dT/dx_{s} is the thermal gradient in the crystal. By substituting Eqs. 29.2, 29.3, and 29.4 into Eq. 29.1 we find

$$Ak_{\text{s}} \frac{dT}{dx_{\text{s}}} = A\rho_{\text{s}} \Delta H_{\text{fus}} \frac{dx}{dt} + Ak_{\text{L}} \frac{dT}{dx_{\text{L}}} \tag{29.5}$$

Upon rearranging

$$\frac{dx}{dt} = \frac{1}{\rho_{\text{s}} \Delta H_{\text{fus}}} \left(k_{\text{s}} \frac{dT}{dx_{\text{s}}} - k_{\text{L}} \frac{dT}{dx_{\text{L}}} \right) \tag{29.6}$$

If the pulling rate exceeds the value of *dx/dt* given by Eq. 29.6 the crystal separates from the melt; if it less than that given by Eq. 29.6, then *A* will increase. Figure 29.5 shows the rings that develop around a single crystal as it grows with *dx/dt* constantly changing to keep *A* constant.

According to Eq. 29.6 the maximum growth rate possible occurs when dT/dx_{L} approaches 0 (if dT/dx_{L} becomes negative the liquid would be supercooled and the interface would advance rapidly and dendritic growth would occur). The maximum growth rate, $(dx/dt)_{\text{max}}$, is then given by

$$\left(\frac{dx}{dt} \right)_{\text{max}} = \frac{1}{\rho_{\text{s}} \Delta H_{\text{fus}}} \left(k_{\text{s}} \frac{dT}{dx_{\text{s}}} \right) \tag{29.7}$$

We can see from Eq. 29.7 that the value of $(dx/dt)_{\text{max}}$ depends on the temperature gradient in the solid. The largest gradients in the solid may be obtained by deliberately introducing large heat leaks from the growing crystal; one method is to water-cool the seed holder. However, the high rates obtained under such conditions are generally not

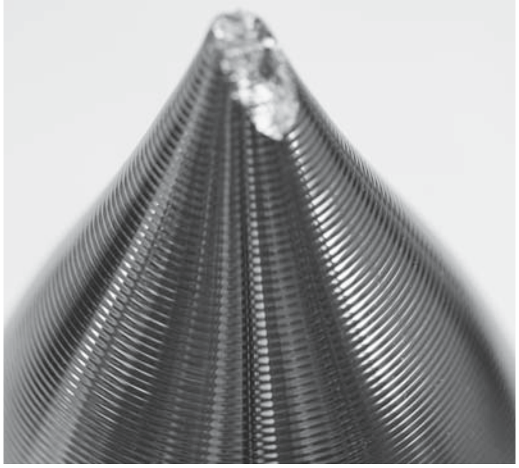


FIGURE 29.5 Growth rings on crystal surface: top section of Si crystal after removing seed.

useful because the crystal perfection under such growth conditions is usually not very high. Typically, growth rates for good crystal quality are 10^{-4}–10^{-2} mm/s, 30–50% slower than the maximum values given by Eq. 29.7.

The Cz process has the following principal advantages:

- Excellent control over the growth conditions produces very high quality crystals.
- It is relatively fast.
- Very large crystals can be produced.

A particular feature of the Cz process is that it is possible to produce dislocation-free single crystals. As discussed in Chapter 12, dislocations are not equilibrium defects. Therefore it is, in principle, possible to produce crystals that are free of dislocations. Although a small number of dislocations in a single crystal of most ceramics does not normally present any problems, this must be avoided if we are using the ceramic for its electrical/semiconducting properties. Dislocation-free crystals can be achieved once growth has started on the seed if the diameter of the crystal is slowly reduced to a minimum size. The minimum size is the size that can still support the weight of the crystal to be grown (without deforming plastically and multiplying the number of dislocations). Typically the minimum size is ~3 mm in diameter and 30 mm long; a 3-mm-diameter sapphire rod will support ~200 kg. During this period, the crystal-melt surface becomes strongly concave as illustrated in Figure 29.6 so that dislocations present in the initial seed can glide to the sidewalls of the crystal. Dislocation glide is facilitated if the glide plane makes a large angle to the growth axis. For crystals with a diamond-cubic structure the glide plane is {111}; for crystals with a rocksalt (NaCl) structure the glide plane is {110} (unless it is not—see Section 17.2). Subsequent growth is slowly modified to give the desired crystal diameter and a dislocation-free crystal is then pulled. The dislocation density in Cz sapphire boules is typically in the range of 10^3–10^4 cm^{-2}.

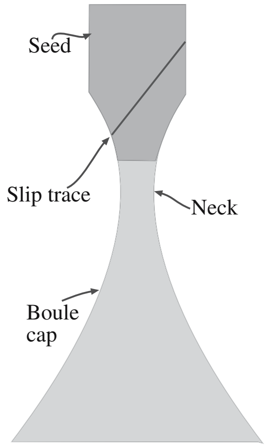


FIGURE 29.6 Schematic illustration of neck-down and flare-out geometries for growing dislocation-free crystals.

There are several disadvantages to the Cz process.

- It is applicable only to materials that melt congruently or nearly congruently (see Sections 8.10 and 29.10).
- The melt must be contained in a crucible; this is a problem for reactive high-temperature melts.
- The capital cost is high. A Cz furnace used to produce 8-inch-diameter sapphire boules costs $400,000. For larger boules the furnace can cost $1 million.

Despite these disadvantages the Cz technique is the most important crystal-growth technique for producing large high-quality single crystals.

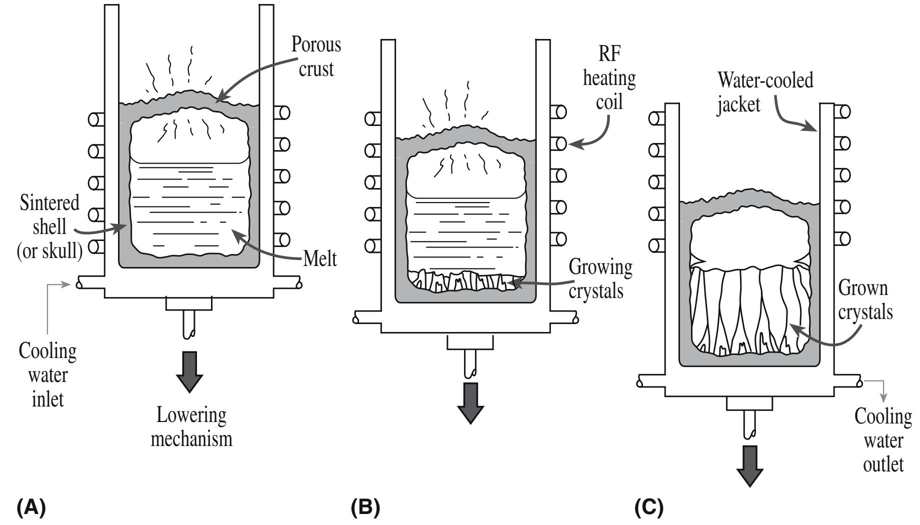
29.7 MELT TECHNIQUE: SKULL MELTING

One of the problems with growing single crystals of ceramic materials is that they often have very high melting temperatures. When molten, the liquid can be extremely corrosive to any crucible. In skull melting the melt is contained within a frozen shell of the material itself—the material acts as its own crucible. In perhaps the first application of the skull melting process the technique was combined with crystal pulling to produce single crystals of manganese ferrite. Later (1961) the same method was successfully applied to the growth of single crystals of sapphire and YAG. [The technique is also known as induction skull melting (ISM) and is used for casting Ti and Ti alloys—for the same reason.]

The most important economic application of the skull melting technique for ceramics has been the production of cubic zirconia (T_M = 2700°C), which is manufactured at rates in excess of 300 tonnes (1.5 billion carats) per year. Cubic zirconia is the best of the diamond simulants and the growth of large (centimeter-sized) crystals became feasible only with the use of the skull melting technique (Figure 29.7). The zirconia powder containing some small pieces of Zr metal is contained in a water-cooled assembly and heated by means of high-frequency induction heating (see Section 9.6). The Zr metal is used to couple with the high-frequency radiation. Once the temperature has reached 1100°C the zirconia becomes electrically conducting and itself acts as a susceptor. The material close to the water-cooled walls remains solid, thus forming a dense sintered shell or "skull." The rest of the zirconia liquefies. To induce crystallization, the melt is lowered slowly (~1 cm/h) from the heating coil, as shown in Figure 29.7b. Crystal growth begins at the base of the melt and large columnar crystals (to ~7 cm long) can be produced.

The cost of cubic ZrO_2 crystals varies depending on supply and demand. The selling price for single crystals is only ~$0.80 g^{-1}. This makes them a low-cost commodity material for the gem trade and necessitates large-scale production to make the process economically feasible. However, once the crystals have been oriented, cut, and polished for use as substrates for thin-film growth (e.g., the high-temperature superconductors) the equivalent cost

FIGURE 29.7 (a–c) The skull melting process.



is ~\$150 g^{-1} [~\$50 for a single 1 × 1 × 0.05-cm-thick (100) oriented substrate].

29.8 MELT TECHNIQUE: BRIDGMAN–STOCKBARGER

The Bridgman–Stockbarger technique is illustrated in Figure 29.8. The powdered charge is melted in a crucible, which is often a refractory metal Pt, Ir, or Mo. This technique necessitates that the melt does not significantly react with the crucible. The furnace is designed such that there is a sharp drop in temperature just below the bottom tip of the crucible in its initial position.

The crucible is lowered (typically at a rate of 1 to 30 mm/h) so that the tip enters the colder zone causing the nucleation of crystals. The crystals grow fastest in particular crystallographic directions and crystals growing at angles greater than half the cone angle terminate at the walls of the cone; only those crystals oriented so that the growth is favored in the axial direction persist into the bulk of the charge as the crucible is lowered into the cooler zone. As a result the upper part of the crucible finally contains either a single crystal or a few large crystals. One of the problems associated with the Bridgman–Stockbarger method occurs if the crystal expands on freezing (this happens in covalently bonded crystals Si and Ge—as it does with ice). The crucible acts as a constraint on the growing crystal and the expansion usually leads to large stresses, which can result in the introduction of dislocations and low-angle grain boundaries (GBs) and even cause the crucible to burst. It is difficult to produce single crystals with dislocation densities less than $10^4\,cm^{-2}$ by this technique. There are other geometries for the Bridgman–Stockbarger technique. One configuration is the horizontal configuration in which the crystal is grown horizontally in a boat.

The Bridgman–Stockbarger method has been used primarily in the growth of alkali halides and alkaline-earth halides (e.g., LiF and CaF_2). Table 29.5 summarizes some

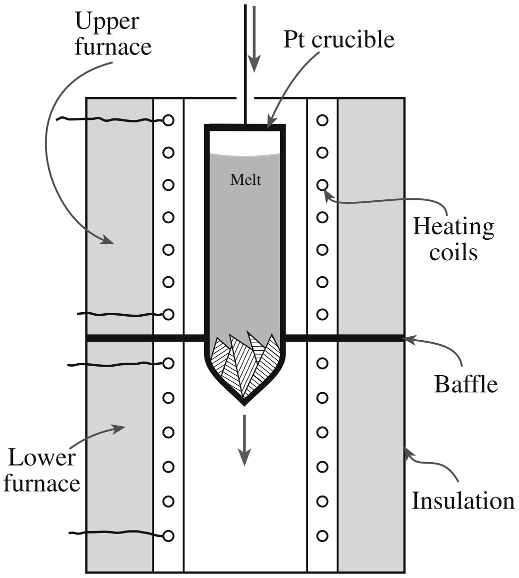


FIGURE 29.8 The Bridgman–Stockbarger technique.

TABLE 29.5 Typical Conditions for Bridgman–Stockbarger Growth

Crystal	T_M *(°C)*	*Growth rate (mm/h)*	*Crucible*
Al_2O_3	2037	2–8	Molybdenum
ZnS	1850	0.5–2	Silica supported by graphite
$FeAl_2O_3$	1790	5–10	Iridium
GaAs	1238	2–6	Sand-blasted silica
Cu	1083	6–60	Graphite powder
Ge	937	50–150	Graphite- or carbon-coated silica
As	814	5–12	Thick-walled silica
AgBr	434	1–5	Pyrex
$NaNO_2$	271	3–6	PTFE[a]
K	63.7	1–4	Stainless steel coated with paraffin
Ar	–189.2	0.7–1.5	Mylar

[a] PTFE, polytetrafluoroethylene.

of the other crystals that have been grown by this method. This table is by no means complete; indeed, several thousand different crystals have been reported. In many cases the furnace tube is filled with an inert gas to protect the charge and crucible. If the crystal is volatile, and the crucible is silica or pyrex, the crucible may also be sealed.

29.9 MELT TECHNIQUE: HEAT-EXCHANGE METHOD

The heat-exchange method (HEM) (also known as the Schmid–Viechnicki method) is best known for its use in growing large crystals of sapphire. Sapphire crystals of 34 cm diameter and 65 kg in weight are grown in a production facility, up from the initial 20 cm diameter, 20 kg weight. (These values should be compared to a maximum diameter of 15 cm for Cz growth.) Sapphire is particularly challenging since it is essential to use low thermal gradients during growth and cool down to prevent cracking of the boule. The furnace is shown schematically in Figure 29.9. The furnace has several special features:

- Heat extraction and input can be controlled independently.
- The boule can be annealed *in situ* after growth.
- Nothing moves mechanically.

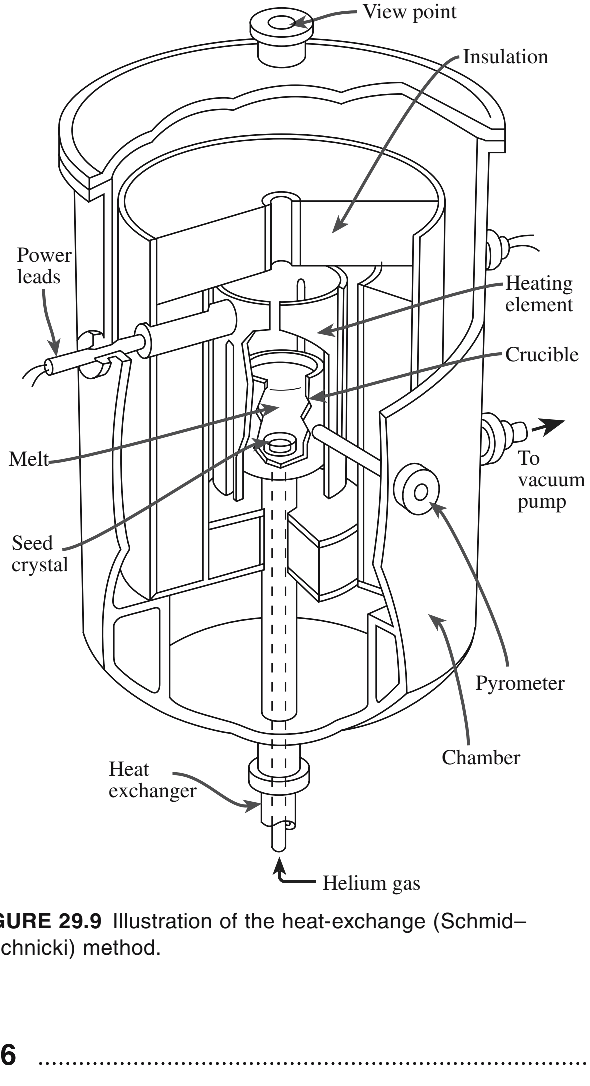


FIGURE 29.9 Illustration of the heat-exchange (Schmid–Viechnicki) method.

In the HEM technique, the Mo crucible, the seed, the melt, and the growing crystal are all located in the heat zone. Heat is removed using a W He-gas heat exchanger and is thus a temperature gradient technique (TGT). The technique uses directional solidification of the melt from a seed that is in contact with the heat exchanger placed at the base of the crucible. The furnace elements melt the sapphire crackle and control the temperature of the liquid. The temperature of the seed is allowed to increase to melt back its surface and then growth begins by lowering the temperature of the seed and the melt. Crystallization is a three-dimensional process. The whole process takes about 72 hours and is followed by a similar annealing period. Growth of (0001) boules is most difficult because the solid/liquid interface is convex toward the liquid in the HEM process, which increases solidification stresses. The situation can be remedied by carefully controlling the temperature gradients. The resultant boule has a flat top surface making a large fraction suitable for preparing windows, etc.

Fluorite crystals for use in ultraviolet (UV) ($\lambda = 193$ nm) and vacuum ultraviolet (VUV) (vacuum UV; $\lambda = 157$ nm) lithography up to 20 cm diameter have been grown using a modified TGT, which is another variation on the directional solidification approach to crystal growth. The inner diameter of the high-purity graphite crucible used is 300 mm. An interesting feature of this method is the use of 2 wt% PbF_2 to scavenge oxygen impurities. Blocks of the CaF_2/PbS_2 mixture are pressed into the crucible with a (111) seed at the bottom. The vacuum is kept at ~10^{-3} Pa with a graphite lid on the crucible to minimize vaporization and the thermal gradient can be controlled by changing the position of the crucible in the furnace or adjusting the flow of cooling water to the bottom of the crucible support. Crystals of CaF_2 up to 250 mm diameter can also be grown by the Bridgman method. In either case, a temperature of ~1500°C is used for the growth.

29.10 APPLYING PHASE DIAGRAMS TO SINGLE-CRYSTAL GROWTH

An important consideration in the crystal growth of oxides containing several cations is whether the melting is congruent or incongruent. The discussion in this section builds on that in Section 8.10. If the compound melts congruently then crystal growth will proceed easily. For example, the crystal could be grown by the Cz method in a way similar to growth of an elemental crystal.

Crystals of lithium niobate, $LiNbO_3$, can be readily grown using the Cz process. Its large nonlinear optical coefficients have led to an intense interest in this material. Figure 29.10 shows part of the Li_2O–Nb_2O_5 phase diagram. The congruent melting temperature is not exactly at the

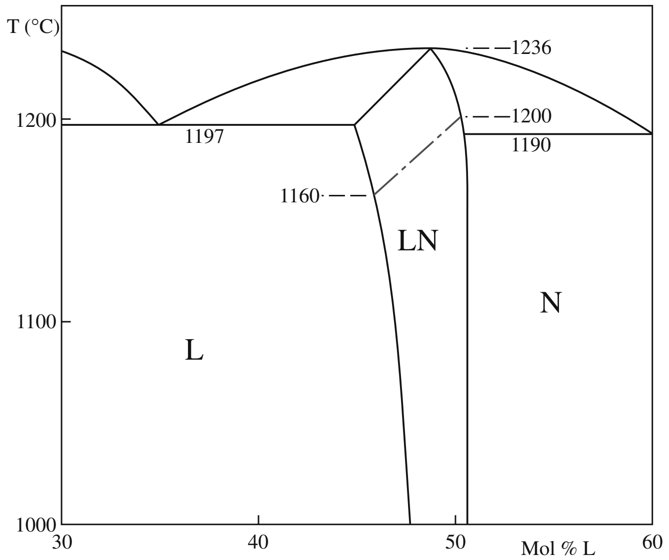


FIGURE 29.10 Part of the Nb_2O_5–Li_2O phase diagram.

stoichiometric composition but at 51.4 mol% Nb_2O_5. Solidifying a melt of the composition 48.6% Li_2O and 51.4 mol% Nb_2O_5 can produce a high-quality single crystal, but the cation stoichiometry will not be 1 : 1. To obtain stoichiometric $Li_{1.00}Nb_{1.00}O_3$ it is necessary to cool a melt containing excess Li_2O. For example, referring back to Figure 29.10, a melt of composition 55 mol% Li_2O and 45 mol% Nb_2O_5 will solidify below ~1200°C producing a stoichiometric solid. During growth of the crystal the melt will become depleted in Nb. To counteract this loss it is necessary to ensure the melt is homogenized by stirring; if a large melt volume is used, and a moderately sized crystal is grown, the composition change will be small.

AUTOCLAVE

An autoclave is a thick-walled vessel, usually made of steel, which allows us to carry out reactions under pressure and at high temperatures. (The original definition implied a self-closing vessel with internal pressure sealing its joints; the closure is now made externally.)

As noted in Section 8.10, pure cubic $BaTiO_3$ cannot be grown from a melt of that composition because, as shown in Figure 8.23, the hexagonal phase is in equilibrium with the liquid at the solidification temperature (1618°C). The hexagonal phase transforms to the cubic phase at 1460°C, but the phase change is very slow and thus the hexagonal phase can persist at room temperature. The hexagonal form of $BaTiO_3$ is not ferroelectric. Its structure contains the required TiO_6 octahedra, but the linking of the octahedra is different from that found in cubic $BaTiO_3$. In cubic $BaTiO_3$ the octahedra share corners; in hexagonal $BaTiO_3$ some of the octahedra share faces.

Cubic $BaTiO_3$ can, however, be grown from a melt composition containing 35 mol% BaO and 65 mol% TiO_2, which solidifies below 1460°C, the temperature below which the cubic form is stable. The melt is held just above its solidification temperature, a seed crystal is dipped into its surface, and the crystal is pulled from the melt at a rate of 0.5–1.0 mm/h. The seed crystal is rotated during growth so that the liquid near the crystal does not become depleted in Ba. Only a fraction of the melt can be obtained as single-crystal $BaTiO_3$ since the whole of it solidifies, forming a mixture of cubic $BaTiO_3$ and $Ba_6Ti_{17}O_{40}$, when the BaO content falls to about 32 mol%.

If the desired compound melts incongruently it is often easier just to use a technique like flux growth to obtain single crystals.

29.11 SOLUTION TECHNIQUE: HYDROTHERMAL

In the hydrothermal method single crystals are grown from an aqueous (hydro) solution. Although many crystals have been grown hydrothermally, α-quartz crystals are the only ones that are produced on a large scale. For this reason we will describe the method used for growing large α-quartz crystals, although the system used for other materials (including emerald and ruby) is very similar. An important feature is that the low-symmetry form of quartz is produced directly since *T* is low.

Pure finely divided particles of mineral quartz are placed at the bottom of a tall cylindrical autoclave that is 80% filled with a basic solution, for example, 0.5 M NaOH. Suitably oriented seed crystals of α-quartz are held in wire frames near the top of the autoclave.

Thermometers allow temperature control within the chamber. The seed crystals are usually naturally occurring quartz, since this usually has a very low dislocation density. The base of the autoclave is kept at 400°C; in this section the quartz fragments dissolve so it is called the *dissolving* section. The top of the autoclave, which is called the *growth* section, is maintained at a temperature some 40°C cooler than the dissolving section. The α–β transition in quartz occurs at 573°C. For highly perfect single crystals, growth should be carried out below the transition temperature. The solution at the bottom of the autoclave will saturate and move by convection to the growth zone where the seed crystals are located. In the growth zone the solubility is lower, the solution becomes supersaturated, and material is deposited onto the seed crystals. Figure 29.11 shows a schematic of an autoclave used for hydrothermal growth. The baffle shown in the lower half of the autoclave is a perforated metal disk separating the dissolving and growth sections and helping to localize the temperature differential. For piezoelectric applications, the principal faces of the seed crystals are {0001} and the crystals grow at ~1 mm/day in both <0001> directions producing crystals weighing over a kilogram in a few weeks. Figure 29.12 shows a hydrothermally grown α-quartz crystal. Table 29.6 lists other ceramic

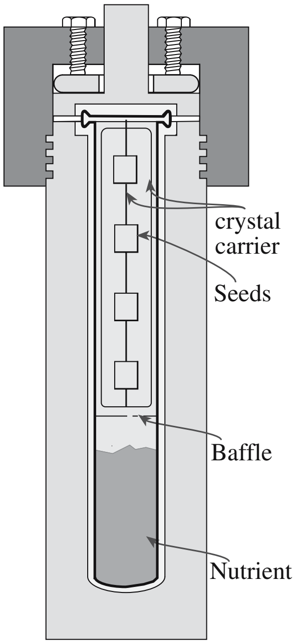


FIGURE 29.11 A silver-lined laboratory hydrothermal autoclave, about 35 cm long. It can be much longer.

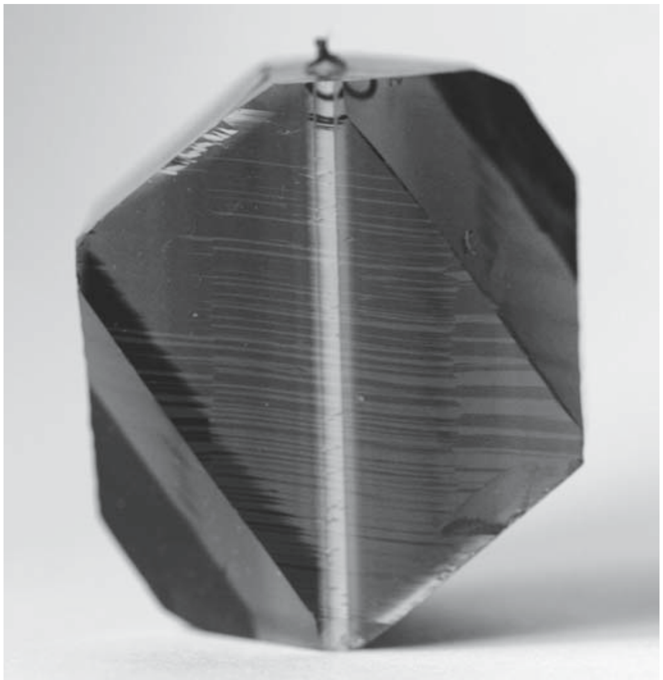


FIGURE 29.12 Hydrothermally grown quartz crystal; note the colorless seed and the Pt support wire at the top.

TABLE 29.6 Examples of Hydrothermally Grown Crystals

Crystal	*Solvent*	*Growth zone temperature (°C)*	*Dissolution zone temperature (°C)*	*Pressure or degree of fill*
α-SiO_2	1 N Na_2CO_3	360	400	80%
	1.0 M NaOH + 0.025 M Li_2CO_3 + 0.1 M Na_2CO_3	374	397	88%
$LiGaO_2$	3.5 M NaOH	385	420	70%
$BiTi_2O_{12}$, $Bi_{12}TiO_{20}$	KF	550~600	—	>70~80%
K(Ta,Nb)O_2	15 M KOH	650	690	1000 atm
$KNbO_3$, $KTaO_3$	KOH	400~600	450~680	70~80%
$PbTiO_3$, $PbZrO_3$	KF	570	585~590	50~55%
$Pb(Ti_xZr_{1-x})O_3$	>10 wt% KF	580	~618	83%
$R_9Al_3(BOH)_2Si_4O_{19}$	H_3BO_3 + NaCl or NaF	400~700	—	1000~3000 atm
$AlPO_4$, $GaPO_4$	6.1 M H_3PO_4, 3.8 M ADP	150	300	80%
$(Mn,Fe,Zn)_8[Be_6Si_6O_{24}]S_2$	1% NaOH or 8% NH_4Cl	450	480~500	1500~2000 atm
Na_2ZnGeO_4	30 wt% NaOH	250~300	253~310	50~90%
$NiFe_2O_4$	0.5 N NH_4Cl	470~480	—	70~75% (1100~1300 atm)
Fe_3O_4	10 M NaOH	500	550	1000 atm
$ZnFe_2O_4$	NaOH	400	—	—
$Y_3Fe_5O_{12}$	1~3 M Na_2CO_3 or 1~3 M NaOH	400~750	—	200~1350 atm
	20 M KOH	350	360	88%
$Y_3Ga_5O_{12}$	1~3 M Na_2CO_3 or 1~3 M NaOH	400~500	—	1000–3000 atm
	K_2CO_3	500	550	~1000 atm
α-Al_2O_3	2~3 M Na_2CO_3 or 1 M K_2CO_3	390~490	500~540	75~82% (1100~1600 atm)
	10% K_2CO_3 or 10% $KHCO_3$	530~600	540~640	50~70%
	4 M K_2CO_3	370	390	85%
	HCl	—	—	—
$Y_3Al_5O_{12}$	2 M K_2CO_3	550	600	1000 atm
$CaWO_4$	4 wt% NaOH	380	430	60~70%
$SrWO_4$, $BaWO_4$	7~10 wt% NaOH	410~485	450~500	70%
	5~7 wt% NH_4Cl or 15~20 wt% LiCl or 30~40 wt% NaCl	430~485	450~500	65~70%
$CdWO_4$	7 wt% NH_4Cl or 16~25 wt% LiCl	430~455	450~470	75%
$SrMoO_4$, $BaMoO_4$	5~7 wt% NH_4Cl or 15~20 wt% LiCl or 30~40 wt% NaCl	430~485	450~500	65~70%
ZnO	5.45 M KOH + 0.7 M LiOH	353	467	83%
PbO	1 N LiOH	430	450	60%
ZnS	2~5 M NaOH	350~380	410~560	50~80%

single crystals grown by the hydrothermal method and the experimental conditions used.

29.12 SOLUTION TECHNIQUE: HYDROTHERMAL GROWTH AT LOW TEMPERATURE

Low temperatures are suitable for nanowires etc. because they do not have to grow very large! An example is the growth of ZnO nanorods. The early stage of growth on a sapphire substrate is shown in Figure 29.13. The principle of the synthesis is the hydroxylation of Zn^{2+} ions in an aqueous solution in the presence of hexamethylenetetramine [HMTA: $(CH_2)_6N_4$].

The hydrolysis reactions are

$$(CH_2)_6N_4 + 6H_2O \Rightarrow 6HCHO + 4NH_3 \qquad (29.8)$$

$$NH_3 + H_2O \Rightarrow NH_4^+ + OH^- \qquad (29.9)$$

This promotes the hydroxylation of Zn^{2+} ions in solution to form dissolved complexes, which are precursors to nucleation of the ZnO precipitate phase.

$$n\left[Zn(H_2O)_p\right]^{2+} \xrightarrow{OH^-} \left[Zn_n(H_2O)_{np-m}(OH)_m\right]^{(2n-m)+} \xrightarrow{OH^-} nZn(OH)_m \qquad (29.10)$$

Though this route has been used for the synthesis of ZnO nanorods in solution, crystal growth can occur on substrates when they are exposed to the vapor phase above a dilute aqueous solution containing 0.025 M $Zn(NO_3)_2$ and 0.025 M HMTA maintained in the range 70–90°C for 1–3 hours.

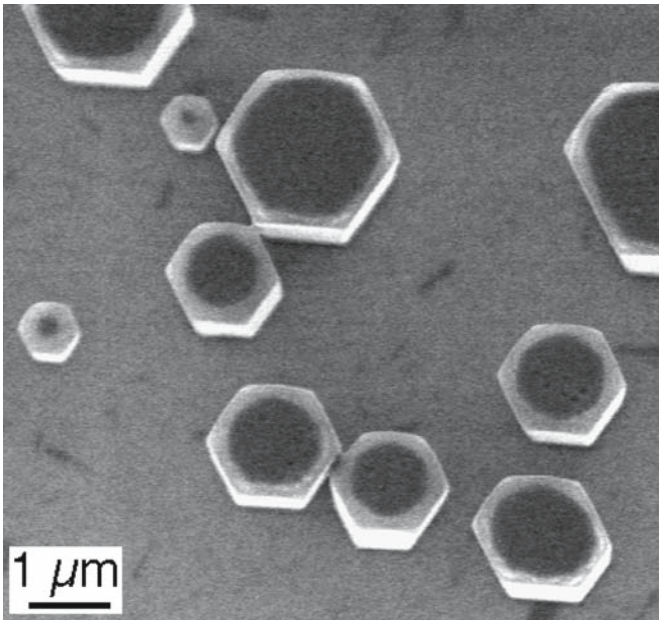


FIGURE 29.13 Hydrothermal ZnO nanorods seen nearly end on.

29.13 SOLUTION TECHNIQUE: FLUX GROWTH

Crystals of many ceramics can be obtained by cooling a solution of the required compound in a suitable flux or solvent (serving the role of water in Section 29.11). The common fluxes include KF, PbO, and PbF_2. The flux is selected to give minimum contamination:

- PbO and Bi_2O_3 are good fluxes for the growth of oxides because Pb and Bi atoms are so large that they do not fit into many lattices.
- Alkali metal ions do not fit well into many lattices either because the sizes or the charges are wrong.

To illustrate the flux-growth process for growing single crystals we will look at three examples.

Pb WARNING

If the temperature is much above 1350°C PbO is reduced to Pb and this can alloy with the platinum crucible!

Yttrium iron garnet ($Y_3Fe_5O_{12}$ or YIG) is ferromagnetic. Approximately 52.5 mol% PbO, 44 mol% Fe_2O_3, and 3.5 mol% Y_2O_3 are mixed together in a Pt crucible and heated to 1250–1350°C. After the melt has homogenized it is cooled at a rate of 0.5°C/h. The solidified melt contains crystals of Fe_2O_3, $PbFe_{12}O_{19}$, and the required $Y_3Fe_5O_{12}$. The mixture is crushed and digested in nitric acid to free the crystals from the flux. In any flux-growth process it is important to have a solvent that dissolves the flux but does not affect the desired crystals. The crystals are separated magnetically at temperatures above and below the appropriate Curie temperatures. The garnet crystals are equiaxed and can also be picked out of the crushed mixture visually.

$BaTiO_3$ crystals have been prepared using a KF flux containing 30% $BaTiO_3$. The mixture is homogenized at 1150–1200°C for about 8 hours. The temperature is then lowered to 900°C and the flux is poured off. The $BaTiO_3$ crystals are allowed to cool in the furnace to room temperature. A characteristic feature of flux-grown $BaTiO_3$ crystals is that they form pairs of triangular plates ("butterfly twins") as shown schematically in Figure 29.14. The cooling rate determines the plate thickness making it possible to form thin sheets directly, without them having to be cut from larger single crystals. In some cases a small amount of iron, about 0.2 wt% Fe_2O_3, is added to the starting mix. Iron assists in the formation of large area plates. However, a small amount of Fe^{3+} is then incorporated in the $BaTiO_3$ lattice on Ti^{4+} sites. The charge difference is compensated for by the replacement of an equivalent number of O^{2-} ions by F^- ions.

Although many details of the process used are kept secret, emeralds [$Be_3Al_2(SiO_3)_6$] can be produced by dissolving BeO, Al_2O_3, and SiO_2 in an Li_2O–MoO_3 flux using

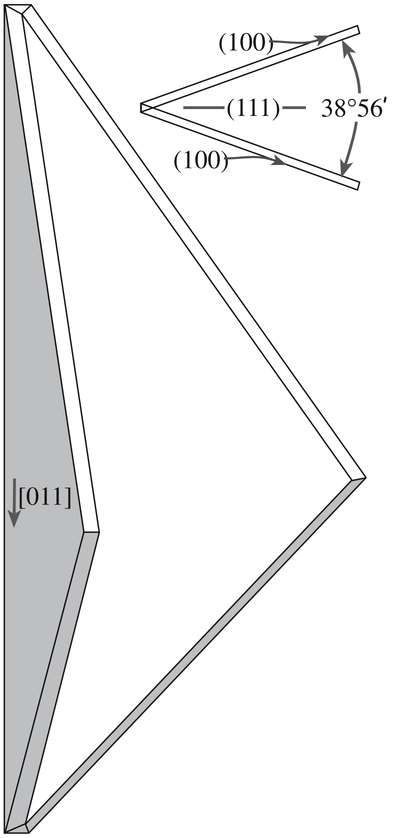


FIGURE 29.14 Butterfly twins in $BaTiO_3$.

an arrangement shown in Figure 29.15; emeralds can grow to ~60 g in 10–12 months. Synthetic rubies can be produced using a PbF_2 flux; rubies can grow to 600 g in 8 months. The synthetic crystals are ~10% of the price of natural ones. The primary commercial manufacturer of emerald and ruby in the United States is Chatham in San Francisco, which produces 20% (1 t/year) of the worldwide production of synthetic emeralds and about 70% (700 kg/year) of the worldwide production of flux-grown rubies.

The main advantage of the flux-growth method is that it can be used for a wide variety of materials. Single crystals of materials that undergo phase transitions, melt incongruently, or have a high vapor pressure at their melting temperature can all be grown using flux growth. The major disadvantages are as follows:

- Impurities may be trapped in the crystal.
- Growth is slow compared to melt-growth methods.
- Growth of very large crystals is not possible.

For these reasons flux growth is a useful research tool for growing small crystals (typical crucible volumes between 50 and a few hundred cubic centimeters), but it is not used widely for the production of industrial single crystals apart from gemstones. Many ceramics have been produced as single crystals by the flux-growth process. The literature contains a large amount of information about suitable fluxes for several thousand materials. Table 29.7 gives a few examples.

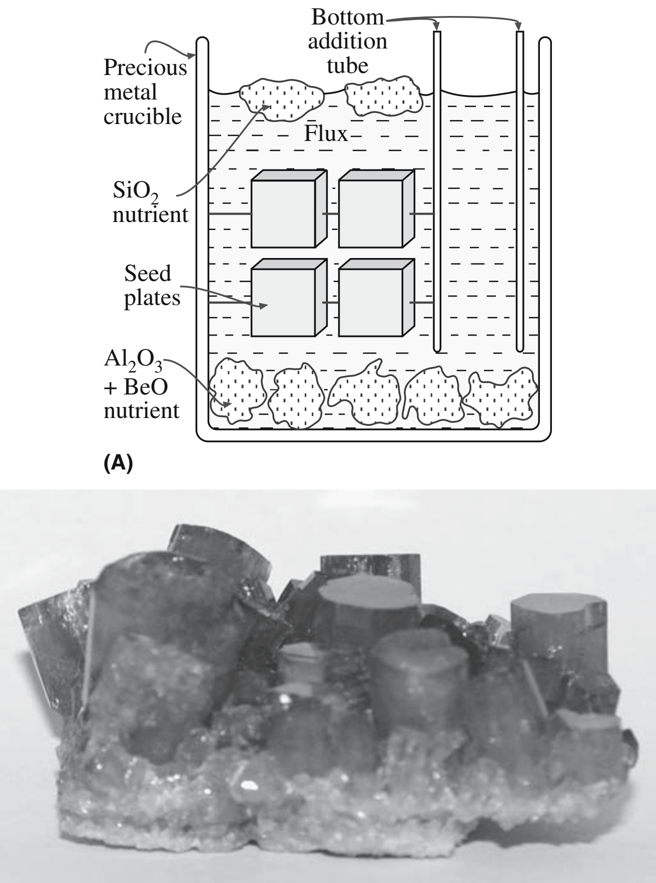


FIGURE 29.15 Flux growth of emerald: (a) schematic; (b) emeralds.

TABLE 29.7 Fluxes Used for the Growth of Ceramics

Material	*Flux*
Al_2O_3	$PbF_2 + B_2O_3$
B	Pt
$BaFe_2O_4$	Na_2CO_3
$BaTiO_3$	Bi_2O_3
$BeAl_2O_4$	PbO, Li_2MoO_3, $PbMoO_4$
CeO_2	$NaF + B_2O_3$
Fe_2O_3	$Na_2B_4O_7$
GaAs	Ga, Sn
$GaFeO_3$	$Bi_2O_3 + B_2O_3$
GaP	Ga
Ge	In, Sn + Pb
GeO_2	$Li_2Mo_2O_7$, $Li_2W_2O_7$
$KNbO_3$	KF, KCl
$KTa_xNb_{1-x}O_3$	K_2CO_3
$MgFe_2O_4$	$Bi_2O_3 + B_2O_3$
$NiFe_2O_4$	$Na_2B_4O_7$
$PbZrO_3$	PbF_2
SiC	Si
TiO_2	$Na_2B_4O_7 + B_2O_3$
$Y_3Al_5O_{12}$	$PbO + B_2O_3$, $PbO + PbF_2$
$Y_3Fe_5O_{12}$	PbO, $PbO + PbF_2$, $BaO + B_2O_3$
ZnO	PbF_2
ZnS	ZnF_2
ZnTe	In, Ga, Sn, Bi, Pb

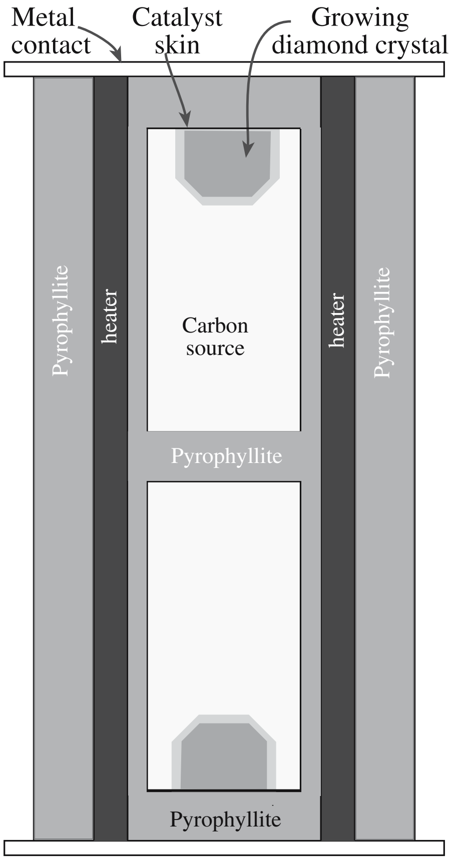


FIGURE 29.16 Chamber for diamond growth.

29.14 SOLUTION TECHNIQUE: GROWING DIAMONDS

In addition to their importance in jewelry, diamonds also have important industrial applications such as in diamond-impregnated cutting tools and as abrasives. The world use of diamonds is about 26 t (26 Mg) per year, of which about 16 t is synthetic. The synthetic diamond industry is a $1 billion/year business.

The carbon phase diagram was shown in Figure 8.7. From this diagram you can see that diamond is in fact the metastable form of C under ambient conditions, with graphite being the stable form. Diamond is stable at pressures as low as 1 GPa if *T* is ~25°C, although the rate of the transformation is extremely slow if the pressure is lower. However, diamonds can be synthesized from graphite at very high temperature (~3300 K) and very high pressure (~13 GPa). A more practical method involves the use of a solution (the flux again) and shares similarities with the other solution methods described above.

The credit for the first synthesis of diamonds goes to Bundy *et al.* of the General Electric Company, although the Swedish company ASEA may have synthesized diamonds in 1953. In each case, the product was diamond grit suitable for grinding and polishing uses. In 1970 researchers at GE succeeded in synthesizing large (up to about 1 ct in weight) single-crystal diamonds. The arrangement for growing large diamonds is shown in the schematic diagram in Figure 29.16. The pyrophyllite (a hydrous aluminum silicate) tube is inserted into a ring of tungsten carbide through which the hydraulic pressure is applied. Pyrophyllite is used because at high temperature and under high pressure it extrudes to form a gasket that bonds well to the tungsten carbide pistons and seals the tube to maintain the applied pressure. Heating is achieved by passing an electric current through the tube. The temperature gradient within the tube is such that the center is between 10 and 30°C hotter than the ends. The carbon source (any carbon-containing compound may be used, even peanuts) is dissolved in the solvent, often Ni, Fe, or an Ni–Fe alloy. The solvent forms a thin film on the surface of the seed and transport of carbon from the source to the crystal takes place by temperature-difference solution growth (similar to what happens in the hydrothermal process). The diamond seed crystals favor the formation of diamond instead of graphite. Growth rates depend on the solvent and the orientation of the seed crystal, but are 3 to 5 mm/day.

29.15 VAPOR TECHNIQUE: VAPOR–LIQUID–SOLID

The VLS mechanism was first used to grow Si whiskers. (Other whiskers were identified some years earlier.) The catalyst-mediated whisker-growth process is illustrated in Figure 29.17 for the growth of SiC whiskers. The process begins with melting a solid catalyst particle (e.g., steel), so that it forms a liquid ball on a suitable surface (in this case, a graphite slab). The ball forms a liquid interface between the growing SiC whiskers and the vapor phase. Carbon (in the form of methane CH_4) and silicon (in the form of SiO) in the vapor feed are extracted by the liquid catalyst, which in turn becomes supersaturated. Crystal growth occurs by precipitation from the supersaturated liquid at the solid–liquid interface. Whiskers produced by the VLS process characteristically have a spherical cap.

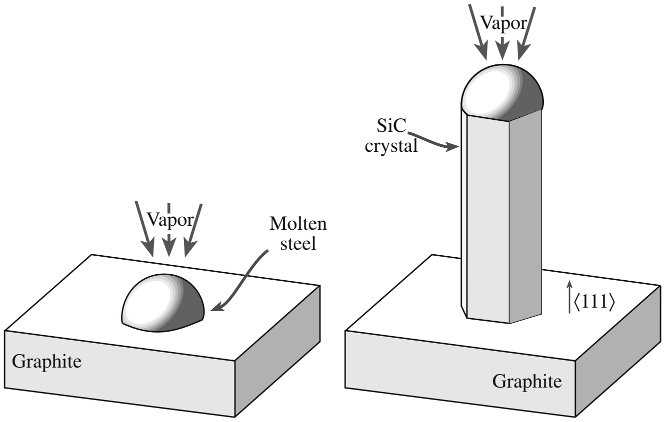


FIGURE 29.17 VLS process for growing SiC whiskers.

One of the drawbacks of the VLS process is that it is extremely slow. This leads to high production costs and limited availability, which together combine to make the whiskers extremely expensive ($800/kg in 1994). Also although SiC has been classified as a nonhazardous material, there are health concerns associated with very small whiskers. This problem may be even more important with the increasing production of the smaller whiskers known as nanowires and nanotubes.

The VLS mechanism has been identified in the growth of other ceramic whiskers including Al_2O_3, BeO, and B_4C. It has been proposed as a method for producing nanotubes, and is often assumed to be the principal feature of such growth processes.

29.16 VAPOR TECHNIQUE: SUBLIMATION

Single crystal SiC is of interest for a number of applications including high-temperature electronic devices and blue-light-emitting diodes. For these applications the preparation of large high-quality boules is necessary from which individual wafers can be sliced. At atmospheric pressure SiC sublimes, so single crystals cannot be produced by melt growth techniques such as the Cz process. However, a sublimation technique has been developed that can produce boules up to 30 mm in diameter. The cross section of a reaction chamber is shown schematically in Figure 29.18. A seed crystal and a polycrystalline source material are placed at opposite ends of a cylindrical container, along which a temperature gradient of 10–20°C/cm is established (2300–2500°C at the source and 2100–2200°C at the seed). SiC sublimes from the source and the products condense onto the cooler seed. The process is carried out at a low argon pressure (200 Pa), allowing boules of 20 mm in length and up to 30 mm in diameter to be produced at a rate of about 4 mm/h.

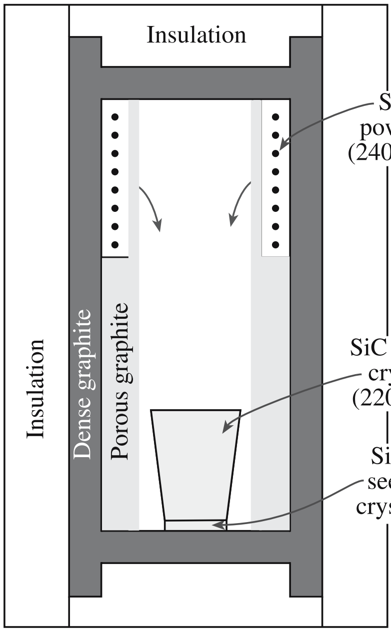


FIGURE 29.18 Modified sublimation process for SiC single crystals.

SiC wafers produced from the boules are very expensive. A single SiC wafer 30 mm in diameter and 0.3 mm thick can cost upward of $3000. By comparison, an Si wafer of this size costs less than $20.

29.17 PREPARING SUBSTRATES FOR THIN-FILM APPLICATIONS

Conversion of the boule into polished substrates requires several operations. The exact number and type of steps involved in this process depend on the material involved and the application for the substrates. The following sequence would be typical for the preparation of single-crystal substrates of ceramics.

- The top and bottom (sometimes called the *seed* and *tang* ends, respectively) of the boule are removed using a diamond-tipped saw.
- The surface orientation of the boule is determined by an X-ray method (typically Laue back-reflection). The boule is mounted in such a way that when it is cut the slices have the desired surface orientation.
- Wafers are sliced from the boule using a diamond-tipped saw or a set of diamond-coated wires. When the wire saw is used many slices can be cut in one run (like slicing a hard-boiled egg). The substrate thickness essentially depends on the slicing operation, although the final value depends on subsequent polishing operations.
- The wafers are polished (see Section 18.12).
- The wafers are diced up to produce individual substrates of the desired size. In some cases the substrates are cut so that the edge is aligned along a particular crystallographic orientation. This orientation is also set by X-ray methods.

29.18 GROWING NANOWIRES AND NANOTUBES BY VAPOR–LIQUID–SOLID AND NOT

There is great interest in growing single crystals that are smaller than 100 nm in one, two, or three dimensions. The techniques being used are variations on those listed above but deserve separate mention because of the special features involved. The detailed mechanisms involved in the growth are not fully understood. The essential feature is that the "substrate" is small.

The VLS technique has probably attracted most attention. Essentially this is an extension of that used by Wagner and Ellis to grow the original Si whiskers, which were themselves nanowires. Vapor–liquid–solid growth of

Si required a catalyst particle, but not all wire growth requires a heterogeneous catalyst. We can grow arrays of ZnO wires by depositing islands of catalyst on a substrate and providing a vapor so that the wires will grow only where the catalyst particle is. In some cases, it appears that the catalyst may be solid throughout the process. In other similar processes there is no catalyst. Nature grows rutile and asbestos fibers sing crystal anisotropy.

Carbon nanotubes started the excitement in nanotechnology, although the Nobel Prize was awarded for the buckyball (Chapter 7). We can construct these nanotubes by rolling the sheet of graphite shown in Figure 29.19a (known as a graphene sheet) and joining the sides. Now we can join the sheets so that A meets B, or C meets D, but we can also make A meet E. You will realize that this corresponds to the formation of a screw dislocation that runs along the tube and really does have a hollow core! Then we could wrap other sheets around the first (not necessarily of the identical construction). The tubes can be grown by several methods include arc-discharge and pulsed-laser deposition; both methods can produce quite large quantities; it has been claimed that tons of high-quality nanotubes will be produced (which will be needed for the space elevator). For technological applications we might prefer to grow arrays of aligned tubes. We can do this using Fe-oxide particles as the catalyst and 9% acetylene in N_2 as the feedstock; the growth temperature need only be ~600°C. Such aligned structures can already be grown from the pores of mesoporous SiO_2, on glass substrates, porous Si, porous alumina, etc. Ni catalysts have been used with plasma-assisted CVD at 660°C. We can use the C nanotubes themselves as templates (or substrates) to grow tubes (or wires) of other materials.

We can now grow tubes of many ceramics. The array of TiO_2 nanotubes shown in Figure 29.19b was grown from a Ti foil placed in an electrolyte of 0.5% HF in water using a Pt cathode. The anodization voltage was kept at

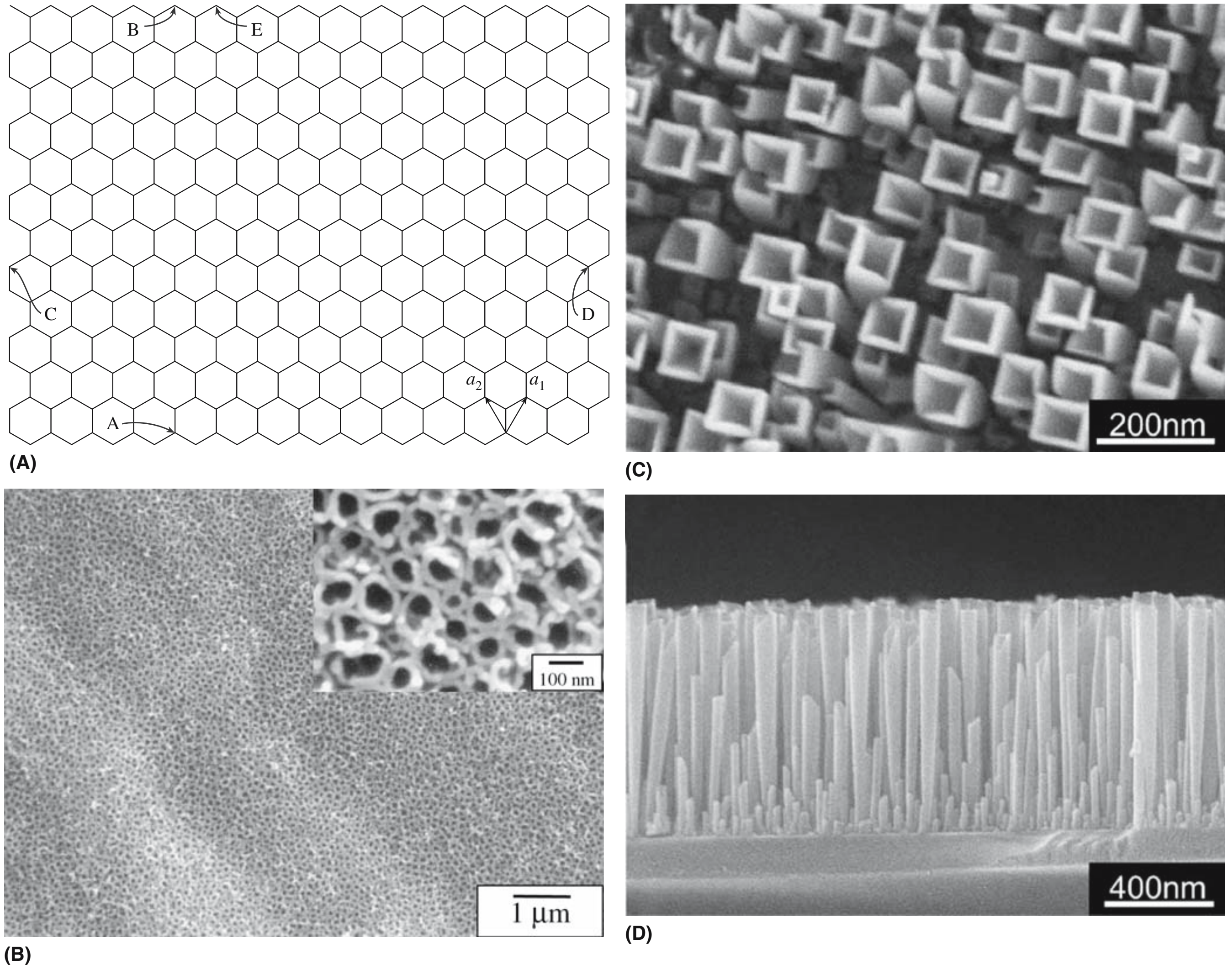


FIGURE 29.19 (a) Graphene sheet illustrating how carbon nanotubes are formed. (b) TiO_2 nanotubes. (c) and (d) IrO_2 nanotubes.

~20 V and this structure was produced in ~45 minutes. The sample was cleaned in pure water and sintered at up to 880°C transforming the as-grown anatase to rutile. The resulting material has many possible applications (it resembles MCM-41 structurally) since it has all the chemical properties of rutile. The nanotubes of IrO_2 in Figure 29.29c and d have a square cross section because they are single crystal with sides parallel to {001} planes. We can grow nanotubes of other oxides such as MgO and NiO, and nanotubes of nonoxides such as BN.

CHAPTER SUMMARY

Many methods can be used to grow single crystals of ceramic materials. To produce large crystals the methods can be classified as melt growth, solution growth, or vapor growth. For solution growth a suitable solvent must be found for the material. Because it is possible to find a solvent for most materials (the literature contains solvents for several thousand materials), solution-growth techniques are applicable to a very wide range of ceramics. Melt-growth techniques generally require that the material melts congruently or nearly congruently—so knowledge of the phase diagram for the material is important—and this fact alone eliminates many materials from consideration. The significant advantage of melt-growth techniques is that, particularly in the case of the Cz method, very high quality crystals can be produced. Vapor growth of bulk material is generally used only to produce single crystals of ceramics like SiC that cannot be made by either melt or solution techniques, or for growing nanocrystals.

Many of the methods used for thin-film growth produce single crystals—the emphasis in this chapter is that the crystals "stand alone."

PEOPLE IN HISTORY

Bridgman, Percy Williams was born in Cambridge, Massachusetts in 1882 and joined the faculty of Harvard University in 1908. He is best known for his research on the effects of high pressure on materials and was awarded the Nobel Prize in Physics in 1946 "for the invention of an apparatus to produce extremely high pressures, and for the discoveries he made therewith in the field of high pressure physics." Bridgman made contributions to many fields including crystallography and devised a method for growing single crystals, which bears his name. He died in 1961.

Czochralski, Jan was born on October 23, 1885 in Kcynia, which is now in Poland. He was the eighth child of a carpenter (died 1953). He went to Berlin to study chemistry in 1904 and by 1910 was working on the processing of Cu. The story is that in 1913 he was writing up his notes on a study of crystallizing metals while sitting next to a crucible with molten Sn. Absentmindedly, instead of dipping his pen in the inkpot, he dipped it in the crucible and withdrew it quickly. He observed a thin thread of solidified metal hanging at the tip of the nib. His observation led to a new crystal growth technique, which he published in 1917.

Verneuil, August Victor Louis (1856–1913) was a French chemist who reported his method for growing ruby in 1902.

GENERAL REFERENCES

Brice, J.C. (1986) *Crystal Growth Processes*, Blackie, Glasgow. A clear description of all the major (and most of the minor) techniques used to produce single crystals and a useful discussion on method selection.

Elwell, D. and Scheel, H.J. (1975) *Crystal Growth from High Temperature Solutions*, Academic Press, New York. An excellent place to look for fluxes for crystal growth.

Hazen, R.M. (1999) *The Diamond Makers*, Cambridge University Press, Cambridge. Fascinating; it reads like a novel.

Hurle, D.T.J., Ed. (1994) *Handbook of Crystal Growth*, Vol. 2, *Bulk Crystal Growth*, North-Holland, Amsterdam.

Journal of Crystal Growth. An international journal that publishes articles that deal with all aspects of crystal growth, from nucleation and growth theories to apparatus and instrumentation.

Laudise, R.A. (1970) *The Growth of Single Crystals*, Prentice-Hall, Inc, Englewood Cliffs, NJ. The standard reference for crystal growth; summarizes materials grown by different methods.

Nassau, K. (1980) *Gems Made by Man*, Chilton Book Company, Radnor, PA. An excellent and highly readable account of the techniques used to produce artificial gemstones. Contains lots of history and background information on the processes and their inventors.

Nassau, K. and Nassau, J. (1980) in *Crystals: Growth, Properties, and Applications*, edited by H.C. Freyhardt, Springer-Verlag, New York.

O'Donoghue, M. (1988) *Gemstones*, Chapman & Hall, London. The processing and properties of gemstones. Chapter 10 discusses synthetic and imitation stones.

Scheel, H.J. and Fukuda, T. (2004) *Crystal Growth Technology,* Wiley, Chichester. In Chapter One, this text points out that Czochralski used the Bridgman technique in his laboratory and that the Cz technique should have been called the Teal–Little–Dash technique after the group who first produced large (nearly) dislocation-free crystals of Ge.

SPECIFIC REFERENCES

Aleksandrov, V.I., Osiko, V.V., Prokhorov, A.M., and Tatarintsev, V.M. (1978) in *Current Topics in Materials Science*, Vol. 1, edited by E. Kaldis, North Holland Publishers, Amsterdam, p. 421. Discussion of skull melting.

Bundy, F.P., Hall, H.T., Strong, H.M., and Wentorf, R.H. (1955) "Man-made diamonds," *Nature* **176**, 51. First description of diamond synthesis. Hazen (1999) indicates that synthetic diamonds may have been made prior to this publication from GE.

Ivanov, P.A. and Chelnokov, V.E. (1992) "Recent developments in SiC single-crystal electronics," *Semicond. Sci. Technol*. **7**, 863. On using SiC for blue LEDs.

Keck, P.H. and Golay, M.J.E. (1953) "Crystallization of silicon from a floating liquid zone," *Phys. Rev.* **89**, 1297. First description of the FZ method.

Khattak, C.P. and Schmid, F. (2001) "Growth of the world's largest sapphire crystals," *J. Cryst. Growth* **225**, 572.

Montforte, F.R., Swanekamp, F.W., and Van Uitert, L.G. (1961) "Radio-frequency technique for pulling oxide crystals without employing a crucible susceptor," *J. Appl. Phys.* **32**, 959. First application of the skull melting process combined with crystal pulling to produce single crystals.

Nassau, K. and Van Uittert, L.G. (1960) "Preparation of large calcium-tungstate crystals containing paramagnetic ions for maser applications," *J. Appl. Phys*. **31**, 1508. Describes the first use of the Cz process to grow ceramic crystals ($CaWO_4$).

Pfann, W.G. (1952) "Principles of zone melting," *Trans AIME* **194**, 747. The zone refining process.

Remeika, J.P. (1954) "A method for growing barium titanate single crystals," *J. Am. Chem. Soc*. **76**, 940. Growth of $BaTiO_3$ by flux growth at Bell Labs.

Schmid. F. and Viechnicki, D. (1970) "Growth of sapphire disks from melt by a gradient furnace technique," *J. Am. Ceram. Soc*. **53**, 528.

Stockbarger, D.C. (1936) "The production of large single crystals of lithium fluoride," *Rev. Sci. Instr.* **7**, 133. Described improvements to the Bridgman process.

Tairov, Yu.M. and Tsvetkov, V.F. (1978) "Investigation of growth processes of ingots of silicon carbide single crystals," *J. Cryst. Growth* **43**, 209; (1981) "General principles of growing large size single crystals of various silicon carbide polytypes," *J. Cryst. Growth* **52**, 146. Describing the sublimation technique for growing large boules.

Teal, G.K. and Little, J.B. (1950) "Growth of germanium single crystals," *Phys. Rev*. **78**, 647. Teal and Little of Bell Telephone Laboratories were the first to produce single crystals of Ge and Si by the Cz method.

Tomaszewski, P.E. *Professor Jan Czochralski* (*1885–1953*). http://www.ptwk.org.pl/art2.htm.

Vergés, M.A., Mifsud, A., and Serna, C.J. (1990) "Formation of rod-like zinc oxide microcrystals in homogeneous solutions," *J. Chem. Soc. Faraday Trans.* **86**, 959. Low-T growth of ZnO.

Wagner, R.S. and Ellis, W.C. (1964) "Vapor-liquid-solid mechanism of single crystal growth," *Appl. Phys. Lett*. **4**, 89; (1965) "Vapor-liquid-solid mechanism of crystal growth and its application to silicon," *Trans. Met. Soc. AIME* **233**, 1053. The description of the VLS mechanism. Now used for more than Si.

Ziegler, G., Lanig, P., Theis, D., and Weyrich, C. (1983) "Single-crystal growth of SiC substrate material for blue-light emitting diodes," *IEEE Transact. Electr. Dev.* **ED-30**, 227. (See Tairov *et al*., 1978.)

EXERCISES

29.1 Describe the Verneuil method for producing ruby. What are the advantages and disadvantages of this process?

29.2 Briefly describe how ruby could be produced by the Czochralski (Cz) process. Under what situations, if any, would it be preferable to use the Cz process rather than the Verneuil process for ruby growth?

29.3 Why are crystals of cubic zirconia grown by the skull melting technique?

29.4 There are several different geometries for the Bridgman–Stockbarger method. Comparing the vertical and horizontal geometries, what are the advantages and disadvantages of each?

29.5 Knowledge of phase diagrams is very important for understanding the growth of single crystals from the melt. Using the case of $BaTiO_3$ explain the considerations involved when producing single crystals of incongruently melting solids using melt growth techniques such as the Cz method.

29.6 Why are flux growth methods widely used in the production of synthetic gems? Are there are disadvantages that you can think of in using these methods for this particular application?

29.7 A company wishing to start producing single crystals of AlN has called you in as a consultant. What advice would you give them concerning the type of methods that would be suitable?

29.8 Draw up a list of as many different substrate materials as you can that have been used in the growth of thin films of the high-temperature superconductors. In your list make note of the surface orientation (if it is given) and the surface condition (was it polished, cleaned, annealed, etc.) of the substrate.

29.9 Using the information you gathered for question 29.8 add to your list one method that could be used to produce each type of single crystal from which the substrates were obtained.

29.10 By carefully reviewing the literature, present a detailed discussion of the method of growing diamond using the “flux” method. You should give quantities, diagrams, and references.