SPIE. FIELD GUIDE

Field Guide to
Crystal Growth

Ashok K. Batra
Mohan D. Aggarwal

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Preface

Crystal growth is the art and science of growing crystals that are pillars of modern technological developments. It acts as a bridge between science and technology. Crystals are used in lasers, semiconducting devices, computers, magnetic and optical devices, optical processing applications, pharmaceuticals, and a host of other devices. Crystal growth requires technical skills in chemistry, physics, and materials science.

This *Field Guide* covers the basic phenomena and techniques for growing bulk single crystals of high-technology materials from solution, melt, and vapors. Some techniques for growing crystal in the microgravity environment of space are also presented. The idea of electronic miniaturization was developed during the mid-1950s due to the understanding and growth of doped silicon crystals. In principle, atoms are stacked in three dimensions in saturated solutions, melt, and vapors. It requires knowledge of temperature control, motion control, heating-furnace design, raising and lowering mechanisms, and phase diagrams.

We hope that the included examples inspire readers with ideas to grow new materials for new devices. Any crystal growth process is complex; it depends on many parameters that can interact. The complexity makes it difficult to reproduce a process that is known to work and makes the processing of new materials much more difficult than it appears superficially. Crystal growth is sometimes frustrating, but like other crafts, it can provide great satisfaction.

Ashok K. Batra
Mohan D. Aggarwal
June 2018

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Ashok K. Batra

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Mohan D. Aggarwal

Table of Contents

Table of Contents

Table of Contents

Glossary of Symbols and Notation

0D	Zero dimensional
1D	One dimensional
2D	Two dimensional
3D	Three dimensional
ADP	Ammonium dihydrogen phosphate
AgBr	Silver bromide
AgCl	Silver chloride
Al_2O_3	Aluminum oxide
$Al_2O_3:Cr^{3+}$	Chromium-doped aluminum oxide
B_2O_3	Boron oxide
$BaTiO_3$	Barium titanate
$Ba_xSr_{1-x}Nb_2O_6$	Barium strontium niobate
BBO	β barium borate
BCC	Body-centered cubic
BCT	Body-centered tetragonal
BGO	Bismuth germanium oxide
BS technique	Bridgman–Stockbarger technique
BSO	Bismuth silicon oxide
C_0	Equilibrium concentration
$CaCO_3$	Calcium carbonate
CaF_2	Calcium fluoride
$CaWO_4$	Calcium tungstate
CCD	Charge-coupled device
CLBO	Cesium lithium triborate
CsBr	Cesium bromide
CZ crystal growth	Czochralski crystal growth
FCC	Face-centered cubic
Fe_2O_3	Iron oxide
FES	Fluid experiment system
GaAs	Gallium arsenide
GaN	Gallium nitride
GaP	Gallium phosphide
GaSb	Gallium antimonide
Ge	Germanium
HgCdTe	Mercury cadmium telluride
InAs	Indium arsenide
InSb	Indium antimonide
KDP	Potassium dihydrogen phosphate
KDP(KH_2PO_4)	Potassium dihydrogen phosphate

Glossary of Symbols and Notation

KTP($KTiOPO_4$)	Potassium titanyl phosphage
$LaBr_3$	Lanthanum bromide
LaF_3	Lanthanum fluoride
LAP	L-arginine phosphate
$LaTaO_3$	Lanthanum tantalite
LBO	Lithium triborate
LHFB	L-histidine tetra fluoroborate
$Li_2SO_4H_2O$	Hydrated lithium sulfate
LiF	Lithium fluoride
$LiIO_3$	Lithium iodate
LN($LiNbO_3$)	Lithium niobate
LRO	Long-range order
MgF_2	Magnesium fluoride
MgO	Magnesium oxide
mNA	Meta-nitroaniline
MNA-MAP	Methyl-(2,4-dinitrophenyl)-minopropanoate: 2-methyl-4-nitroaniline
$Na_2B_4O_7$	Sodium borate
NaF	Sodium fluoride
NaI:Tl	Thallium-doped sodium iodide
$NaNO_3$	Sodium nitrate
Nb	Niobium
Nb_2O_5	Niobium oxide
PbF_2	Lead fluoride
PbI_2	Lead iodide
PbO	Lead oxide
PMN-PT $Pb(Mg_{1/3}Nb_{2/3})$ $O_{3-}PbTiO_3$	Lead magnesium niobate—lead titanate
Pt	Platinum
RF	Radio frequency
rpm	Revolutions per minute
RT	Room temperature
RTV	Room-temperature vulcanization
Si	Silicon
Si_3N_4	Silicon nitride
SiO_2	Silicon oxide

Glossary of Symbols and Notation

SnPbTe	Tin lead telluride
SrI_2	Strontium iodide
$SrTiO_3$	Strontium titanate
Ta	Tantalum
TGS	Triglycine sulfate
TiO_2	Titanium oxide
TSSG	Top-seeded solution growth
UV	Ultraviolet
V_m	Molar volume
$Y_3AL_5O_{12}$	Yttrium aluminum garnet
$Y_3Fe_5O_{12}$	Yttrium iron garnet
YAG	Yttrium aluminum garnet
ZnO	Zinc oxide
ZnS	Zinc sulfide
ZnSe	Zinc selenide
ZnTe	Zinc telluride
ZrO_2	Cubic zirconia (zirconium oxide)
β	Surface tension
Δ	Solubility parameter
ΔC	Super saturation
ΔH	Molar enthalpy
ΔT	Super cooling
ΔU	Molar energy
$(NH_2CH_2COOH)_3$ H_2SO_4	Triglycine sulfate

Crystal Growth

A **crystal** is a regular periodic arrangement of atoms in three dimensions. **Crystal growth** is the process of rearranging atoms or molecules in a melt or solution into an ordered solid state. They can be grown from saturated aqueous solutions and melts. Crystals have

- A characteristic geometrical shape,
- Highly ordered 3D arrangements of atoms,
- Planes and faces bounding them,
- Planes that intersect at particular angles, and
- A sharp melting and boiling point.

The creation of high-quality crystals of a suitable size is the first and most important step in determining any crystal structure. This process occurs in two steps: nucleation and crystal growth.

Nucleation may occur at a seed crystal, but in the absence of seed crystals, it usually occurs on a particle of dust or some imperfection in the surrounding crystal growth vessel. Thus, if crystals do not appear to emerge from supersaturated solutions, then seeding must be performed, whereby either microcrystals from a previous attempt are introduced or the glassware is rubbed to induce imperfections in the glassware. The former is not recommended because it may create defects in the crystals.

Crystal growth is the increase in the size of particles and leads to a crystalline state. In other words, the term refers to the subsequent size increase of the nuclei (cluster of particles) that have attained the critical cluster size. Crystal shape depends on the internal symmetry of the material and the relative growth rates of the faces. Rapidly growing faces are usually smaller and less well developed than slower-growing faces.

Objectives of Crystal Growth

The operating capabilities of many modern technological hardware and devices are based on active and/or passive crystalline core pieces, i.e., from nanocrystallites to bulk single crystals. The fabrication of such bulk single crystals usually involves the well-established growth methods named after Bridgman, Czochralski, and Verneuil; zone melting, top-seeded solution growth (TSSG)/flux; recrystallization techniques; etc. The crystal growth from liquid phases plays the most important role. Each step of the growth process is affected by controlling the experimental parameters: pressure p, temperature T, and concentration (of components) xi, correlated with the thermodynamic terms phase, pressure, temperature, and concentration. Crystal growth can be depicted to start in a $p - T - xi$ phase space at any point po, To, xi(o). By default, the final point of the growth process is fixed at normal atmospheric pressure, room temperature, and the desired crystal composition. A phase transition (first order) is needed for a solid/crystalline state: sublimation, solidification, precipitation, or recrystallization.

Additionally, one or more **phase transitions** may exist in the solidified material between the starting and final points. The kinds of solid/solid phase transitions are varied, and the structural quality of the grown crystal is strongly influenced by the type of transitions involved. Ferroelectric compounds play an important role in several technical applications. Thus, ferroelectric phase transitions, classified as a phase transition of the second order, are of special interest for crystal growth, especially in perovskites ($LiNbO_3$, $BaTiO_3$, KNbO3), tetragonal tungsten bronzes (strontium barium niobate (SBN)), and potassium titanyl phosphate (KTP; KTiOPO4).

Phase diagrams represent all of these transitions. The determination, knowledge, and understanding of phase diagrams are essential preconditions for the growth method and process.

Crystallization Methods

All crystallization methods alter the physical state of a material by transforming the system from some nonequilibrium state to an equilibrium state. **Crystallization methods** can be divided into two categories based on the system that performs this transformation:

- **Concentration gradient methods** typically concentrate the solution by either removing solvent or transporting the material to another solvent system in which the material is less soluble.
- **Thermal gradient methods** rely on the fact that crystals form on cooled seed.

The choice of method for a particular sample depends greatly on the physical and chemical properties of the system. High-quality crystals require specially tailored solvents, crystallizing agents, and temperatures.

The material should be as pure as possible. When crystallization attempts consistently yield oils, the material is probably impure. Solvents/co-crystallizing materials should also be as pure as possible.

Most solution methods that require glassware must be thoroughly cleaned.

If the material only yields small crystals, the method should be altered to slow the growth step.

Avoid vibrations near the growing crystals because they change the system to an equilibrium state faster than desired.

When growing crystals with a concentration gradient method, use the smallest amounts of solvent needed to dissolve the material.

Some techniques work in a few hours, and others require weeks or even months.

Synthetic Crystals

Synthetic crystals can be divided into three main types:

Technical crystals represent one of the two largest portions of the single-crystal market. They have commercial and military applications. We eat crystals (salt, sugar), and we use crystals as clocks in digital watches and computers (quartz, SiO_2), for information processing and storage (silicon, Si) for switching televisions (gallium arsenide, GaAs), for telecommunication (gallium arsenide, GaAs), and for transportation (e.g., turbine blades contain nickel–aluminum compounds). Huge salt crystals (CaF_2) are used as UV-light lenses at the submicron level during electronic-device fabrication. Other crystals are used for polarizers, transducers, infrared detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers, nonlinear optics, piezoelectrics, acousto-optics, photosensitive materials, and nuclear sensors, including medical applications.

Synthesized **research crystals** of high quality are the basis of solid state research. They are also required for modern light and particle scattering and for diffraction instruments, such as monochromators and detectors. A broad range of geometrically well-prepared crystals are required for thin films, catalysis, and electrochemical investigations.

Jewelry is the second largest segment of the single-crystal market. Crystals within the earth have always attracted people, and belief in the virtues of gems and some minerals dates back at least two thousand years. Crystalline gems have been used for ornamental purposes since the beginning of human history.

Applications of Single Crystals

Single crystals must meet a certain minimum quality in terms of purity and perfection, and thus they must be grown in controlled conditions.

Semiconductors

- Electrical diodes: Si, Ge, SiC
- Hall effect magnetometer: InSb
- Integrated circuits: Si, GaAs
- Infrared detectors: GaSb, InAs, Hg_xCd_{1-x} Te
- LEDs: GaAs, GaSb, GaP, $Sn_xPb_{1-x}Te$, GaN, ZnTe
- Photodiodes: Si, GaAs, Hg_xCd_{1-x} Te
- Photoconduction devices: Si, Hg_xCd_{1-x} Te
- Radiation detectors: Si, Ge, CdTe, BGO, PbS
- Transistors: Ge, Si, GaAs crystals
- Thyristors: Si

Hard crystalline materials and materials for mechanical components

- Abrasives and cutting tools: SiC, diamond, sapphire (Al_2O_3)
- Bearings: Al_2O_3, Si_3N_4, ruby (Al_2O_3:Cr^{3+})
- Substrates for high-T_c superconductors: $SrTiO_3$
- Strain gauges: Si, Ga(As, P)
- Cantilevers: Si, Si_3N_4

Pyroelectric materials

- Pyroelectric devices: TGS, $LiTaO_3$, $Ba_xSr_{1-x}Nb_2O_6$ (e.g., fire/intrusion alarms, room-temperature IR sensors, and ambient energy harvesting)

Magnetic materials

- Microwave filters: Garnets ($Y_3Fe_5O_{12}$, $Y_3Al_5O_{12}$)
- Tape heads: Ferrites

More Applications of Single Crystals

Optical materials

- Electro-optic devices: $LiNbO_3$, ADP, KDP
- Laser hosts: YAG, $Al_2O_3:Cr^{3+}$ (ruby), alexandrite, $CaWO_4$, Ti:Al_2O_3, GaAs, AlGaAs, InP, InSb, AlGaInP, InGaAsSb, InGaN
- Lenses, prisms, and windows: Al_2O_3 (0.15–55.0 μm), Ge (1.8–22 μm), LaF_3 (0.4–11 μm), Si (1.2–15 μm), CaF_2 (0.12–10 μm), MgF_2 (0.11–8.0 μm), AgBr (0.5–35.0 μm), AgCl (0.4–28.0 μm), LiF (0.12–7.0 μm), CsBr (0.23–45.0 μm), quartz (0.19–4.0 μm), ZnS (0.4–13.5 μm)
- Magneto-optic devices: YIG ($Y_3Fe_5O_{12}$)
- Nonlinear optical devices: ADP, KDP, $LiNbO_3$, KTP, BBO, LBO, CLBO
- Polarizers: $CaCO_3$, $NaNO_3$
- X-ray monochromators: Si, KAP
- Photorefractive devices (e.g., holographic data storage and phase-conjugate mirrors): $BaTiO_3$, $LiNbO_3:Fe^{3+}$, BSO ($Bi_{12}SiO_{20}$)
- Scintillation detectors: NaI:Tl, BGO ($Bi_4Ge_3O_{12}$), $LaBr_3$, SrI_2

Piezoelectric materials

- Resonant bulk-wave devices: SiO_2, $LiTaO_3$
- Surface-wave devices: SiO_2, $LiNbO_3$
- Transducers: Quartz, Rochelle salt, ADP, PZT, ADP
- Ambient energy harvesters: PZT, PMN-PT, TGS crystals

Ferroelectric materials

- Memory devices: PZT
- Energy harvesting

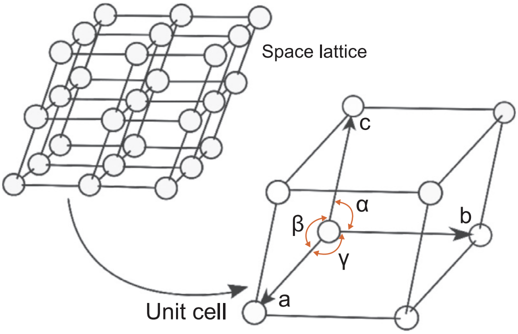
Gems for jewelry

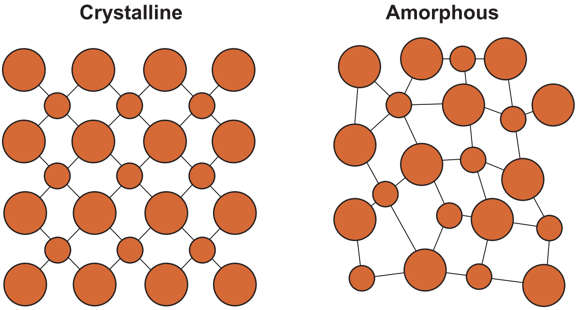
- Cubic zirconia (ZrO_2), diamond, ruby, sapphire (Al_2O_3), moissanite (SiC)

Crystal Structure and Unit Cell

Atoms, arranged in a repetitive 3D pattern, in **long-range order** (LRO, i.e., order in the arrangement of atoms and molecules in the solid extends across large numbers of lattice units or the entire crystal) produce a **crystal structure**. The properties of solids depend on the crystal structure and bonding forces. An imaginary network of lines, with atoms at the intersection of lines, that represents the arrangement of atoms is called a **space lattice**. A **unit cell** is a block of atoms that repeats itself to form a space lattice.

Materials arranged in **short-range order** (SRO, i.e., local ordering of atoms) are called **amorphous materials**.

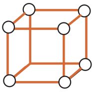




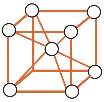
Crystal Systems and Bravais Lattice

There are four types of unit cells (simple, body centered, face centered, and base centered), and only seven different types of unit cells are necessary to create all point lattices: cubic, tetragonal, orthorhombic, rhombohedral, monoclinic, triclinic, and hexagonal.

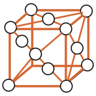
According to Bravais (1811–1863), 14 standard unit cells can describe all possible lattice networks.



Simple cubic

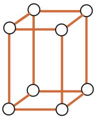


Body-centered cubic (BCC)

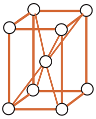


Face-centered cubic (FCC)

Tetragonal: a = b ≠ c, α = β = γ = 90°

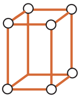


Simple tetragonal

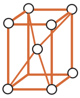


Body-centered tetragonal (BCT)

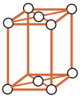
Orthorhombic: a ≠ b ≠ c, α = β = γ = 90°



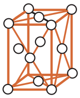
Simple



Body-centered

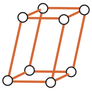


Base-centered

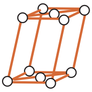


Face-centered

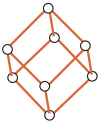
Monoclinic: a ≠ b ≠ c, α = γ = 90° ≠ β



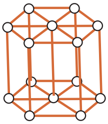
Simple monoclinic



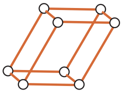
Base-centered monoclinic



Rhombohedral
a = b = c
α = β = γ = 90°



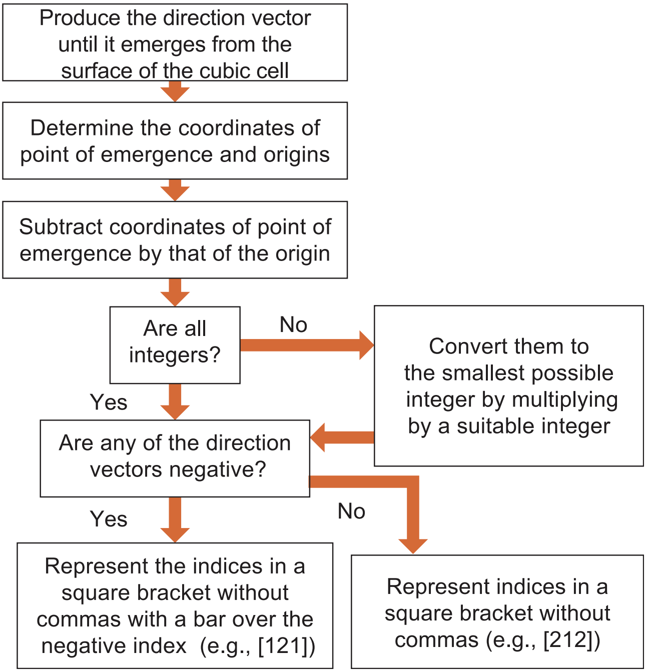
Hexagonal
a = b ≠ c
α = β = 90° γ = 120°



Triclinic
a ≠ b ≠ c
α ≠ β ≠ γ ≠ 90°

Direction Indices

The procedure to find the **direction indices** of a crystal can be portrayed by the following flowchart.



Suppose that the origin coordinates are (3/4, 0, 1/4) and the emergence coordinates are (1/4, 1/2, 1/2).

- Subtract the origin coordinates from the emergence coordinates:

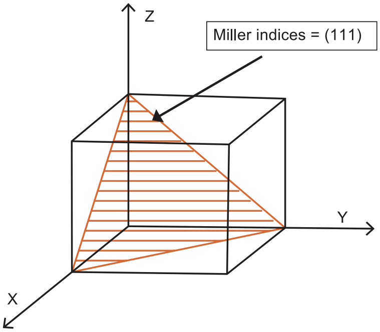
$$(1/4, 1/2, 1/2) - (3/4, 0, 1/4) = (-1/2, 1/2, 1/4).$$

- Multiply by 4 to convert all fractions to integers:

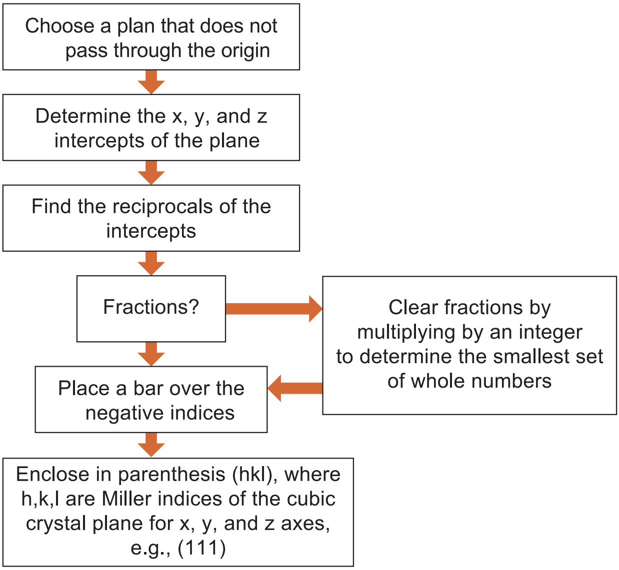
$$4 \times (-1/2, 1/2, 1/4) = (\bar{2}, 2, 1).$$

Therefore, the direction indices are $[\bar{2}\ 2\ 1]$.

Miller Indices



Miller indices are used to refer to specific lattice planes of atoms. They are reciprocals of the fractional intercepts (with fractions cleared) that the plane makes with the crystallographic *x*, *y*, and *z* axes of three nonparallel edges of the cube. The orientation of a crystal plane is defined by determining how the plane intersects the main crystallographic axes of the solid structure. The application of a set of rules leads to the assignment of the Miller indices (*hkl*), a set of numbers that quantify the intercepts and thus may be used to uniquely identify the plane.



Imperfections in Crystals

A perfect crystal is an idealization; there is no such thing in nature. Atom arrangements in real materials do not follow perfect crystalline patterns. Nonetheless, most of the materials that are useful in engineering are crystalline to a very good approximation.

The preferred structures of solids at low temperature are those that minimize energy of the system. Low-energy atomic configurations are almost invariably crystalline because the regular pattern of the crystal lattice repeats whatever local configuration is most favorable for bonding.

Without imperfections, materials would have limited ductility (i.e., malleability) and thus could not be formed into useful shapes. Furthermore, the following aspects are possible due to particular kinds of imperfections:

- increased strength due to impurities or second phases,
- diffusion processes due to vacancies or interstitials, and
- altered mechanical properties (at low and high temperatures) due to grain boundaries.

The following criteria determine the extent of crystal-structure perfection:

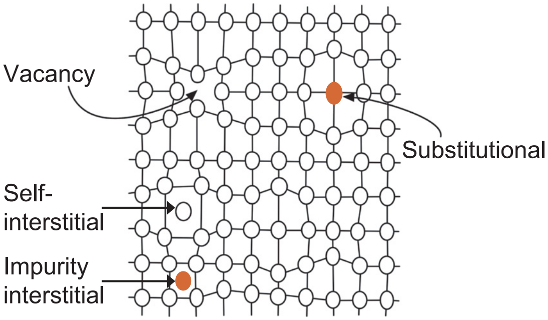
- the density of point defects,
- single dislocations and their accumulations,
- the presence of macroscale and microscale blocks,
- impurity distribution homogeneity, and
- the presence of inclusions and voids.

Types of Imperfections

Crystal lattice defects can be defined by their dimension:

- **Point (0D) defects** affect isolated sites in the crystal structure. They are localized to a few atomic sites. An example is a solute or impurity atom, which alters the crystal pattern at a single point.
- **Linear (1D) defects** are called **dislocations**. They are lines along which the crystal pattern is broken.
- **Surface (2D) defects** are those, such as the external surface and the grain boundaries, along which distinct crystallites are joined together.
- **Planar (3D) defects** change the crystal pattern over a finite volume. They include precipitates, which are small volumes of different crystal structure, and large voids or inclusions of second-phase particles.

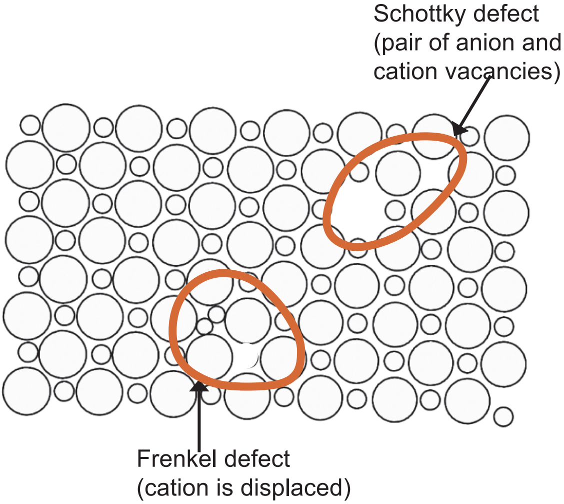
It is important to differentiate **intrinsic defects** (those that appear in a pure material) from **extrinsic defects** (those caused by solute or impure atoms). An intrinsic defect is formed when an atom is missing from a position, thus creating a vacancy, or when an atom occupies an interstitial site where no atom would generally appear, thus creating a **self-interstitial defect**. **Extrinsic point defects** affect engineering properties, which is important in semiconducting crystals, where extrinsic defects are utilized to control electrical properties.



Point Defects

Point defects include two types:

- The **Frenkel defect** involves a single ion, which is displaced from its normal lattice point and shifted to a nearby interstice, or space, between atoms in the lattice. It is defined as a cation–vacancy-cation interstitial pair.
- In the **Schottky defect**, two ions of opposite sign leave the lattice. It is defined as a paired set of cation and anion vacancies.

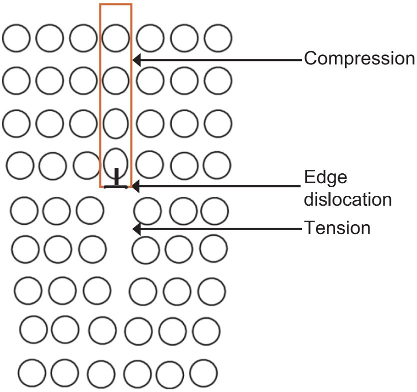


The defects are formed during crystal growth or post-growth treatment, or as a result of external factors. The criteria used to assess the level of crystal structure perfection are the density of point defects, single dislocations and their accumulations, the presence of macroscale and microscale blocks, the impurity distribution homogeneity, and the presence of inclusions.

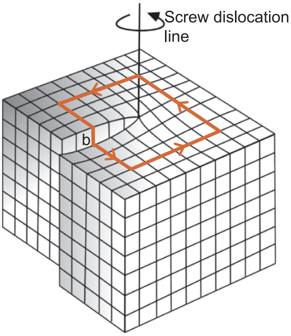
Linear Defects: Dislocations

A **dislocation** is a crystallographic defect or irregularity within a crystal structure. Dislocations are abrupt changes in the regular ordering of atoms, along a line (dislocation line) in the solid. They generally occur in high-density materials and have a large effect on the mechanical properties of the material.

Dislocations are generated if, for example, an extra half plane of atoms is inserted or removed. Such dislocations are called **edge dislocations**.



In **screw dislocations**, atoms are displaced in two separate planes perpendicular to each other.



External Surface and Planar Defects

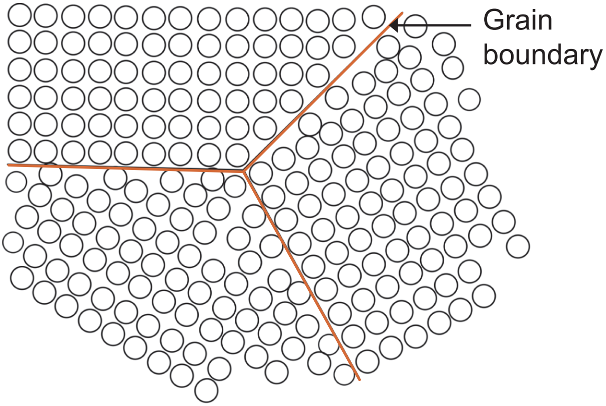
The 2D defects that appear in crystals can be divided into three types:

- **free surfaces**, which are the external surfaces at which the solid terminates at a vapor or liquid;
- **intercrystalline boundaries**, which separate grains or distinct phases within the solid; and
- **internal defects** that disrupt the crystalline pattern over a surface within a crystal.

All of these defects have two important characteristics. First, because they are surfaces in a crystal, they have particular atomic structures that depend on orientation. Second, they have a positive energy. The energy per unit area ordinarily equals the surface tension of the interface.

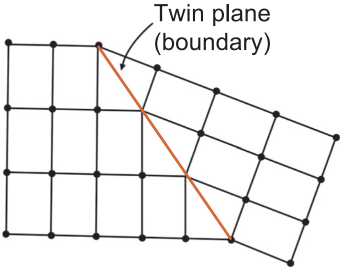
The 3D defects include grain boundaries, crystal twins, stacking faults, voids, and precipitates.

Grain boundaries occur when the “internal” surfaces that separate grains (crystals) of different orientation are created in metals during solidification, when crystals grow from different nuclei. Atomic packing is lower in the grain boundary compared to the crystal grain, which can also be partially amorphous.



Crystal Twins and Stacking Faults

A **twin boundary** is a special type of grain boundary across which there is specific mirror lattice symmetry; that is, atoms on one side of the boundary are located in mirror image positions of the atoms on the other side.



The region of material between these boundaries is appropriately termed a **twin**. Twins result from atomic displacements that are produced from applied mechanical shear forces (mechanical twins) or during annealing heat treatments following deformation (annealing twins).

Low-energy twin boundaries with mirrored atomic positions across the boundary may be produced by the deformation of materials. This behavior produces **shape-memory metals**, which can recover their original shape if heated to a high temperature. Shape-memory alloys are twinned, and when deformed they untwin. At high temperature, the alloy returns to the original twin configuration, thus restoring the original shape.

A **stacking fault** is a defect in the sequence of planes of atom positions in the crystal, like so:

$$\text{FCC}: \ \ldots\text{ABCABC}\ldots$$

$$\ldots\text{ABCABABCABC}\ldots \ \text{Stacking fault}$$

A stack of close-packed planes in the order …ABCABC… generates the FCC structure. A stacking fault occurs wherever this pattern is broken. For example, in a crystal with the local stacking sequence …ABCBABC…, the extra B plane in the middle creates a stacking fault.

Voids and Atomic Vibrations

A **void** is defined as the absence of a number of atoms to form internal surfaces; similar to microcracks, other defects exist in all solid materials that are much larger than those discussed thus far. Voids include pores, cracks, foreign inclusions, and other phases. They are normally introduced during the processing and fabrication steps. Some of these defects affect the properties of materials.

Atomic vibrations occur even at zero temperature (a quantum-mechanical effect) and increase in amplitude with temperature. In fact, the temperature of a solid is a measure of the average vibrational activity of atoms and molecules. Vibrations transiently displace atoms from their regular lattice site, which destroys the perfect periodicity. In a sense, these atomic vibrations may be thought of as imperfections or defects.

At room temperature, a typical vibrational frequency of atoms is on the order of 10^{13} vibrations per second, whereas the amplitude is a few thousandths of a nanometer. Many properties and processes in solids are manifestations of this vibrational atomic motion. For example, melting occurs after the atomic bonds are overcome by vigorous vibrations.

3D defects are defined as either extended defects, e.g., pores, or volume defects, e.g., cracks. A typical volume defect is porosity, often introduced in the solid during processing. A common example is snow, which is highly porous ice. The presence of volume defects can greatly affect the electrical, mechanical, thermal, and optical properties of a material.

Crystal Growth Processes

The formation of the solid crystalline phase can occur only if some degree of supersaturation or supercooling has been achieved first in the crystal growth system. The crystallization process contains three basic steps:

- Attainment of supersaturation or supercooling;
- Formation of critical sized nuclei, i.e., nucleation; and
- Growth of the nuclei into crystal.

The physical processes for the growth of single crystals, either as bulk materials or in the form of thin films, can be divided into four principle categories:

Solidification: Crystal growth proceeds by means of a liquid-to-solid phase transition representing the freezing of a molten phase. Commonly referred to as “melt growth.”

Precipitation: Crystal growth proceeds by the establishment of a supersaturated condition for a solute in a solvent, leading to the deposition of a solid phase. Commonly referred to as “solution growth.”

Condensation: Material in the gas phase is transported to a cooler region and then deposited to form the solid state. Commonly referred to as “vapor growth” or “vapor transport.”

Transformation: The solid–solid transition of a material to enlarge existing small crystalline grains to form larger crystals (as in the case of the “strain/anneal process”), transform material in the amorphous state into the crystalline state (as in the process of devitrification), or epitaxially re-grow amorphous layers formed on the surface of a crystal by heavy particle irradiation.

How to Choose the Method (Liquid to Solid Phase)

The driving force behind crystal growth is the deviation from equilibrium, expressed by ΔC (supersaturation) or ΔT (supercooling):

$$\Delta C = (dC_o/dT)\Delta T$$

where dC_o/dT is the temperature coefficient of solubility, and C_o is the equilibrium concentration of solution.

- If dC_o/dT differs appreciably from zero, crystallization should be achieved by changing the solution temperature.
- If $dC_o/dT \approx 0.1$ g/liter · K, then the temperature-difference methods are preferred.
- If dC_o/dT is high (>1 g/liter · K) but absolute solubility is low, then the temperature-difference methods are also preferred.
- If dC_o/dT is very high (≫1 g/liter · K), then the solution cooling or heating method is used.
- If dC_o/dT is very low (≪1 g/liter · K), then a solvent evaporation technique or chemical reaction/gel technique is necessary.

Low-temperature solution crystal growth (70–90°C) is recommended if

- the materials decompose at their melting temperature,
- the materials melt incongruently,
- a suitable solvent is available, and
- the equipment is inexpensive.

Crystals grown at low temperature have fewer defects.

Solvent Selection

A **solution** is a homogeneous mixture of a solute in a solvent. The solute is the component present in a smaller quantity. For a given solute, there may be different solvents. Apart from high-purity starting materials, solution growth requires a good solvent. The solvent must be chosen by accounting for the following factors:

- high solubility for the given solute with a positive temperature coefficient of solubility,
- good solubility gradient,
- low viscosity,
- low volatility,
- low corrosion, and
- low vapor pressure.

A proper choice of solvent based on knowledge of its chemical reactivity helps one to avoid undesired reactions between solute and solvent. Except that, in general, the solubility of the growth materials in solvents must be sufficiently large, the solubility parameter δ can often be used in estimating the solubility of nonelectrolytes in organic solvents:

$$\delta = (\Delta U/V_\mathrm{m})^{1/2} = (\Delta H - RT/V_\mathrm{m})^{1/2}$$

where V_m is the molar volume of the solvent, ΔU is the molar energy, and ΔH is the molar enthalpy. δ is a solvent property that measures the work necessary to separate the solvent molecules. Often a mixture of two solvents, one having a δ-value higher than that of a solute and the other lower, is a better solvent than either of the two solvents separately. Another property, that is, the dipole moments between the solute and solvent, may also be considered for selecting solvent for crystal growth. Most typical organic solvents have a dipole moment less than about 3 Debye. Therefore, in the case of a solute having a similar value of dipole moment, a much wider choice of solvents is possible.

Solubility

Solubility is an important parameter for crystal growth from solution at a low temperature. Before any solution growth technique can be applied, the congruent or incongruent solubility must be determined, and the absence of compound formation with pure or mixed solvents must be established. In the latter cases, a special compositional and thermal regime will be necessary to crystallize the desired phase. inspection can determine the solubility. Upon cooling, crystallized material is obtained for solid phase analysis. This apparatus is easily fabricated and convenient for measuring solubility:

- The solute and solvent is weighed into a glass ampoule.
- The ampoule is seated and rotated in a bath controlled by a thermostat, the temperature of which is increased in steps of 0.5°C every 1–2 h.
- The final disappearance of the solute yields the saturation temperature. The accuracy of this measurement is within ±0.5°C.

The time needed to reach equilibrium for most covalent organic materials is usually shorter than that of sparingly soluble salts, but the settling times before analyses may be longer. In many soluble salts, such as potassium dihydrogen phosphate (KH_2PO_4, or KDP), triglycine sulfate ($(NH_2CH_2COOH)_3H_2SO_4$, or TGS), and ethylene diamine tartarate ($(CH_2NH_2)_2C_2H_4O_6$, or EDT), the solubility is strongly temperature dependent. However, for some soluble salts, such as $LiIO_3$ and $Li_2SO_4 \cdot H_2O$, the solubility is not dependent on temperature and even has inverse slope. Various techniques can measure solubility, such as those based on the vortex flow caused by concentration and optical effects.

If the solubility is too high, it is difficult to grow bulk single crystals, and if it is too small, solubility restricts the size and growth rate of the crystals.

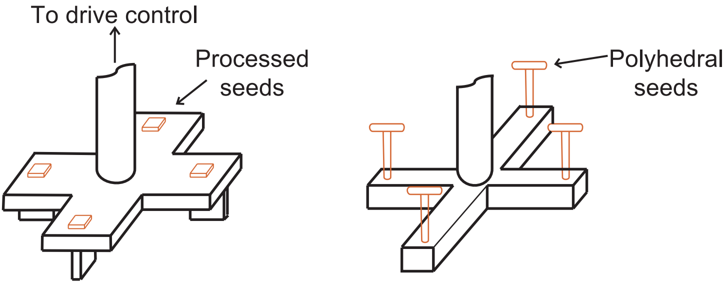
Solubility and Supersaturation

Solubility data at various temperatures is essential to determine the level of supersaturation. Thus, the solubility of the solute in the chosen solvent must be determined before starting the growth process. If the solubility gradient is very small, slow evaporation of the solvent can maintain supersaturation. The growth of crystal from solution is mainly a diffusion-controlled process; the medium must be less viscous to enable faster transference of the growth units from the bulk solution to the growth site by diffusion. Thus, a solvent with less viscosity is preferable. Most important single crystals, such as potassium dihydrogen phosphate (KH_2PO_4, or KDP) and (L)-arginine phosphate monohydrate (LAP), are grown in aqueous solutions or in solvents that are mixtures of water and miscible organic solvents. Of all known substances, water was the first to be considered as a solvent because it is nontoxic, abundant, and low cost.

The accurate measurement of **supersaturation** is usually difficult. Some new methods, such as holographic phase-contrast, interferometric microphotography and trace fluorescent probing, have been developed to measure the concentration distributions and thickness of the boundary layers under different convection conditions with greater accuracy. Although these methods need more development and refinement, they are promising alternatives to determine the supersaturation of easily soluble compounds. If the solubility is known, supersaturation can be calculated by measuring the temperature of the solution and its equilibrium temperature; however, the latter is not always easy.

Seed Crystal Preparation and Mounting

In order to ensure the best growth conditions, a special **crystal holder** should be used because the success of an experiment may depend upon its suitability. The selection of the crystal holder and the method for attaching a seed to it are no less important than the selection of the growth method. A crystal holder should ensure that a seed is held securely in a desired orientation and that it and the growing crystal can be moved in any required manner. The crystal holder should not become deformed due to the selected speed and direction of the motion or due to the weight of the final crystal grown on it. The crystal holder material should be chemically inert in the solution of the substance being crystallized. Two Plexiglas seed holders were specially designed, fabricated, and successfully used for aqueous-solution crystal growth, as shown here. The seed crystals are mounted using a 100% silicon rubber Dow Corning Silastic® 732 RTV adhesive.



A **seed** is a small fragment of a crystal or a whole crystal that is used to start the growth of a larger crystal in a solution. This seed must meet the following requirements to obtain reasonably high-quality crystals:

- It should be a single crystal free of cracks or boundaries.
- It should be free of inclusions.
- Its surface should be free of any sharp, cleaved edges.
- It must be grown under the same conditions as those used to grow the desired single crystals.

Solution Preparation and Starting a Growth Run

Solution preparation requires knowledge of the solubility data of the growth material at different temperatures. Sintered glass filters of different pore sizes are used for solution filtration. The clear solution, saturated at the desired temperature, is poured into the growth vessel. For growth by slow cooling, the vessel is sealed to prevent solvent evaporation. Before starting the crystal growth process, a small crystal suspended in the solution is used to test the saturation. The varying temperature means that neither growth nor dissolution occurs. The test seed is replaced with a good-quality seed (or seeds). All unwanted nuclei and the surface damage on the seed are removed by dissolving at a temperature above the saturation point. Growth is initiated after lowering the temperature to the equilibrium saturation. A controlled solvent evaporation can also be used to initiate the growth. The quality of the grown crystal depends on

- the nature of the seed,
- cooling rate, and
- agitation of the solution.

Various new, nonlinear optical crystals hold promise for use in optical processing devices, e.g., LAP, LHFP, LAFB, MNA:MAP, and L-pyroglutamic acid have been successfully grown using the aforementioned reciprocating system in combination with the temperature-lowering technique.

This simple and versatile crystallization apparatus can be fabricated in any college, university, or scientific laboratory from readily available components.

Design Considerations

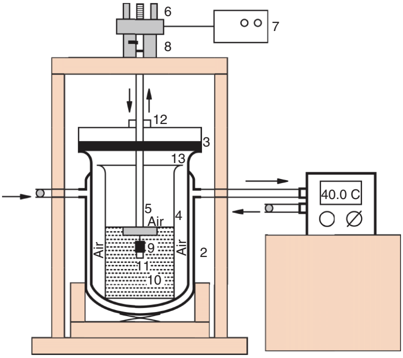
When designing a crystallizer to grow crystals from solution with the temperature-lowering method, the following conditions should be met:

- The operating temperature ranges from room temperature to 80°C, depending on the solvent.
- Hydrodynamic conditions in the solution are set.
- Growth parameters, such as growth rate, are measured.
- Grown crystals can be removed from the crystallizer without any thermal shock.
- The saturation/temperature decrease rate can be changed.
- Different types of seed holders can be used.
- Long-term operating reliability of the system can be established.

Because many solution crystallizers are not available on the market, it is necessary to design and fabricate a system based on one's requirements.

A modified crystallizer can be used to grow large crystals from solutions with a versatile electronic reciprocating control system that changes and reciprocates the motor speed of the seed holding rod. The rotation rate and number of revolutions in the clockwise and counterclockwise direction can be adjusted. This electronic system prevents jerky motions from the seed holder during reciprocation. Good-quality crystals of important, nonlinear optical materials, e.g., methyl-(2,4-dintropheny)-aminopropanoate: 2-methyl-4-nitroaniline (MNA:MAP), LAP, L-histidine tetrafluoroborate (LHFB), and L-arginine tetrafluoroborate (LAFB), and others, such as triglycine sulfate and KDP, have been successfully grown in a laboratory using this system. The complete crystallization apparatus along with the electronic circuit can be easily fabricated in a laboratory with readily available components.

Example System



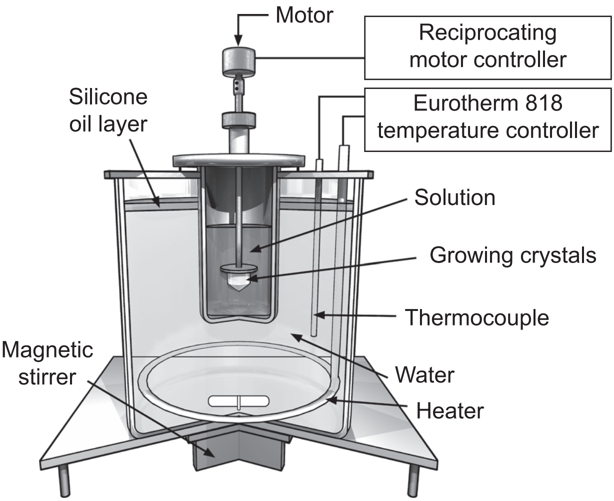
An example of a modified solution-crystal-growth system consists of a 250-ml crystallizer jar (4), which holds the growth solution, placed inside a 2.5-L jacketed kettle (2). The linear and reciprocating motion of the Teflon seed holder (5) is controlled by a rack–pinion arrangement (8) and electronic circuit (7), respectively. A reversible motor (6) is used to rotate the seed holder. The temperature of the solution is controlled and programmed by circulating water with a NesLab bath (1). Evaporation of the solvent is prevented by a specially designed oil Teflon seal (3) and/or RTV/Teflon seal (3). Other elements include a Teflon tape cover (9), solution (10), seed crystal (11), Teflon seal (12), and glass lid (13).

This crystal growth system has the following advantages:

- Better temperature stability, even with sudden fluctuations in temperature, because the solution is in a beaker inside the jacketed vessel (an air gap provides extra insulation).
- Better control over the evaporation of organic solvents (due to an extra lid on the inside beaker and a Teflon seal over the jacketed vessel).
- A mechanical-screw-type arrangement pulls the seed crystal at a controlled rate.
- The ability to vary the seed orientation and type.
- The inner beaker is filled halfway with solution (rather than three-fourths, as usual), so the crystal is annealed *in situ* and spurious aloe-vera-like growth near the seed in some crystals, e.g., MNA:MAP, is either reduced or eliminated.

Alternative System Design

Another system was designed with a reciprocating seed arrangement and other components. It uses a magnetic stirrer to maintain a particular, uniform temperature in the water bath. A layer of silicon oil on the surface of water reduces the evaporation of water to a minimum, which is a significant improvement over earlier designs. Besides temperature control, the uniform rotation of seeds is required to prevent stagnant regions or re-circulating flows; otherwise, inclusions in the crystals will be formed. To study and achieve the uniform and optimal transport of solute to the growing crystals, various seed-rotation mechanisms have been used in the past. Unidirectional rotation of the seed forms cavities in central regions of a crystal face because of reduced solute transport to this region compared to the edges and corner of the growing crystal. Furthermore, non-uniform solute supply favors the formation of defects.



To avoid these defects and stagnant regions in the solution, either eccentric or clockwise and counterclockwise motion of the seed holder is used to grow crystals.

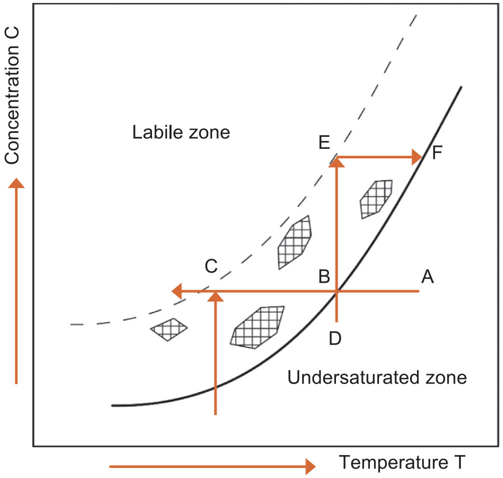
Solid Crystal Growth Methods

The growth of crystal ranges from a small, inexpensive technique to a complex, sophisticated, and expensive process, and crystallization time ranges from minutes to hours, days, or months. Single crystals may be produced by the transport of crystal constituents in the solid, liquid or vapor phase. Based on the phase transformation process, crystal growth techniques are classified as solid growth, vapor growth, melt growth, and solution growth. **Solid-to-solid phase transformations** include the following techniques:

- **Grain growth technique**: The size of the crystalline grain increases when a finely grained material is kept at high temperature for a certain period of time.
- **Strain-annealing technique**: The introduction of strain into the crystal leads to plastic deformation, after which annealing it significantly improves crystallinity. Compression, tension, torsion drawing, and extrusion are employed to strain the samples.
- **Solid-state phase transformation**: A poly- or single-crystalline sample of the undesired polymorph is transformed to the required polymorph through a structural transition. It may be necessary to apply pressure or vary the temperature, or both.

Slow Cooling of Solution

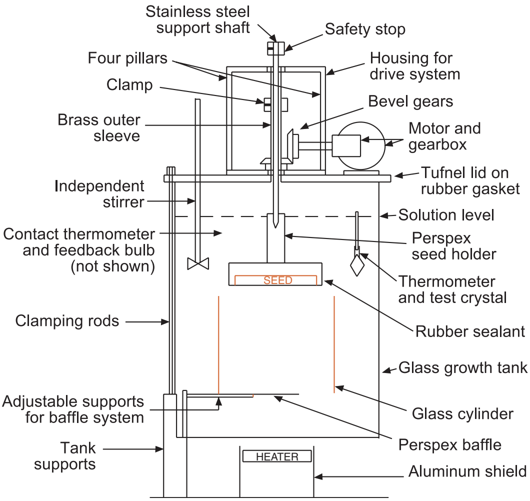
Slow cooling of solution is the best way to grow crystals. The main disadvantage of this method is that it requires a narrow range of temperature, and so much of the solute remains in the solution at the end of the growth run. To compensate for this effect, a large volume of solution is needed. Conversely, a wide range of temperature may not be desirable because the properties of the grown crystal can vary with temperature. With this method, growth occurs without any secondary nucleation in the solution if the supersaturation is fixed within the metastable zone limit. A fast cooling rate changes the solubility beyond the metastable zone width, and multi-nucleation occurs at the expense of the seed crystal. The metstable zone width is the zone between the solubility curve (CE) and nucleation curve (FB). A balance between lowering the temperature and achieving the desired growth rate must be maintained. Growth at a low level of supersaturation prevents strain and dislocation formation at the interface. Supersaturation can be increased after the initial growth reaches a reasonable rate.



The main objective is to create supersaturation without causing spontaneous nucleation in the solution.

Recipe for Triglycine Sulfate Crystals

Triglycine sulfate ($(NH_2CH_2C00H)_3 \cdot H_2SO_4$, or TGS) is one of the most important ferroelectric materials because it is the most sensitive infrared-detecting crystal. Single crystals of TGS are usually grown from aqueous solution with the temperature-lowering or solvent-evaporation method. In our example, the outside water bath, with a capacity of ∼12 L, and the smaller inner cubical growth cell, with a 1-L capacity, consist of Plexiglas. Temperature control of the crystallizer is achieved using a 250-W immersion heater controlled by YSI Model 72 proportional temperature controllers to an accuracy of ±0.1°C. The uniformity of the temperature throughout the bath is achieved with a fluid circulation pump. The bath temperature is monitored at two points during the crystal growth using NBS calibrated thermometers. The crystals were grown by slowly cooling the solution at the desired rate.



TGS crystals are doped with L-alanine to enhance their performance and check depoling for use in an infrared sensor element. A rotating disc technique has been applied uniformly to grow L-alanine-doped TGS crystals using a large-area seed crystal with a large (010) face. A conventional crystallizer was modified to allow growth under suitable hydrodynamic conditions to stabilize growth on the (010) face.

Detailed TGS Crystal Growth Method

When growing crystals from aqueous solutions, the solution must be prepared with a well-determined saturation temperature, solubility profile, and no foreign particles. The following method starts with a solution prepared using high-purity crystalline TGS at a 40ºC saturation temperature. (The solubility of TGS at various temperatures is determined and compared with information available from various sources.)

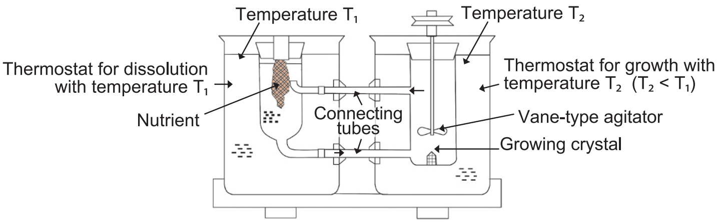
- To prepare the saturated solution, 464 g of TGS is weighed and dissolved in 1000 cc of distilled water.
- The mixture is heated to 50ºC and mixed thoroughly using a Teflon-coated magnetic stirrer.
- The solution is then filtered through a 5-µm filter funnel by a vacuum unit.
- After filtration, this solution is transferred into the growth chamber. The bath temperature is kept at 45ºC at the start of the growth run.
- The solution is poured into the growth cell. The temperature is then reduced to 41.5ºC, 1.5ºC above the saturation temperature, and allowed to stabilize overnight.
- The saturation temperature is again checked by inserting the crystal into the solution and by refractive-index measurements. At each saturation point, the refractive index is measured at a different temperature beforehand with an Abbe refractometer. The starting growth temperature is adjusted based on the result of this procedure.
- Then the seed crystal holder is placed in an oven and heated to 45ºC.
- The preheated seed crystal holder is then inserted into the growth cell and attached to the reciprocating apparatus.
- The seed crystals are slightly dissolved, and the growth run is started.
- The bath temperature is reduced by 0.1ºC/day initially and by 0.2°C/day at the final stage of growth.

Detailed TGS Crystal Growth Method (cont.)

The removal of the grown crystals from the mother liquor requires care. Mishandling may induce defects, thus destroying the scientific value of the crystal, or fracture it altogether. To avoid cracking crystals due to thermal shock, they are wrapped in a lint-free paper towel heated at the final growth temperature. The crystals are then transferred to an oven kept at an appropriate temperature, which is then slowly lowered to room temperature. Grown crystals can be easily removed from the seed holder with slight force applied by fingers, e.g., because RTV 732 adhesive can be used to mount the seed crystal.

Prior to transferal to the growth cell, all precautions were taken to keep the seeds and the holder surface free of dust or foreign particles.

Temperature-Difference Method



Temperature-difference methods are based on the formation of two regions with different temperatures in the crystallizer. In one region, the substance that is always in excess in the form of the solid phase is dissolved, and in the other region, crystal growth occurs.

This method involves the transport of materials from a hot region that contains the solute material to be grown to a cooler region, where the solution is supersaturated and the crystal grows.

This method has several advantages:

- The crystal grows at a fixed temperature.
- Changes in temperature do not affect growth so long as both the source and the growing crystal undergo the same change.
- Economical use of solvent and solute.

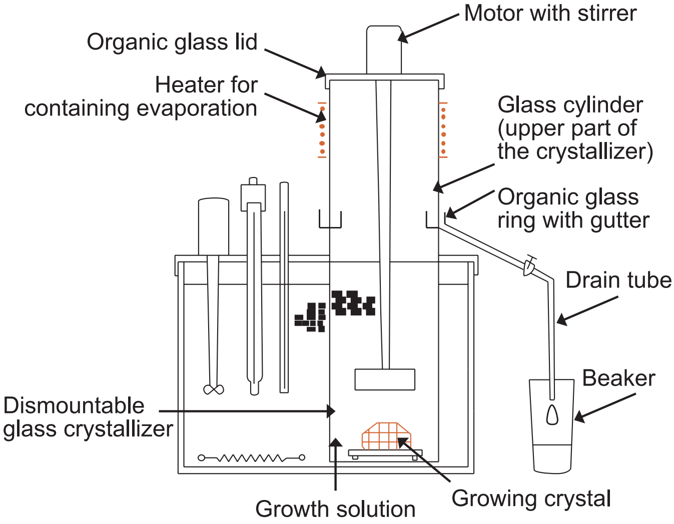
However, changes in the small temperature difference between the source and the crystal zones have a large effect on the growth rate.

Excellent-quality crystals of ferroelectric and piezo-electric materials, such as ammonium dihydrogen phosphate (ADP), potassium dihydrogen phosphate (KDP), and triglycine sulphate (TGS), are commercially grown for use in devices by the low-temperature solution growth method.

Solvent-Evaporation Method

The rate of evaporation is controlled by the position of the heater (the higher is heater is raised, the higher the solvent evaporation per unit time). Supersaturation can be achieved via the **solvent-evaporation method**: as the solvent evaporates, the solute concentration increases above the equilibrium value, thus creating growth. The process is performed at a constant temperature under strictly isothermal conditions. It is similar to the slow cooling method with respect to the apparatus requirements. The temperature is fixed, and provisions are made for evaporation. With nontoxic solvents such as water, it is permissible to allow evaporation into the atmosphere. Typical growth conditions involve temperature stabilization to about ±0.005°C and rates of evaporation of a few ml/hr.

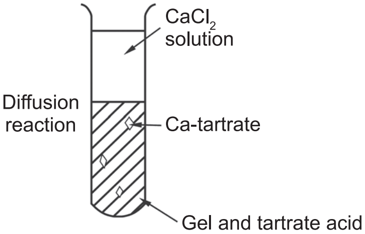
The main advantages of solvent evaporation are that the crystal grows at a fixed temperature and it is insensitive to changes in temperature, provided that both the source and growing crystal undergo the same change and economy of solvent and solute. Conversely, a small temperature difference between the source and the crystal zones has a large effect on the growth rate.



Gel/Chemical Method

The **gel method**, which is the only method that can be used with materials that have a very small temperature coefficient of solubility, is exceedingly simple. One such procedure prepares a gel using a commercial water glass, adjusted to a specific gravity of 1.06 g/cm^3. Gel is then mixed with 1 M of tartaric acid and allowed to gel in a test tube. After the gel is formed, another solution can be placed on top (1-M $CaCl_2$ solution). Over time, crystals of calcium tartrate tetrahydrate are formed in the gel. Essentially, one solution diffuses through the gel and reacts with the other solution to form crystals of appropriate chemicals:

$$H_6C_4O_6 + CaCl_2 \longrightarrow CaC_4H_4O_6 + HCl$$



This technique is useful for low-solubility cases where ionic species are present. The growth rate of a gel method depends on the following factors, among others:

- Gel density (which affects ionic diffusion),
- Concentration of reagents in the gel,
- Concentration of reagents diffused into the gel,
- Temperature, and
- Length of the diffusion path.

Gel-grown crystal sizes range from millimeters to centimeters.

Growth of TGS Crystals in Space

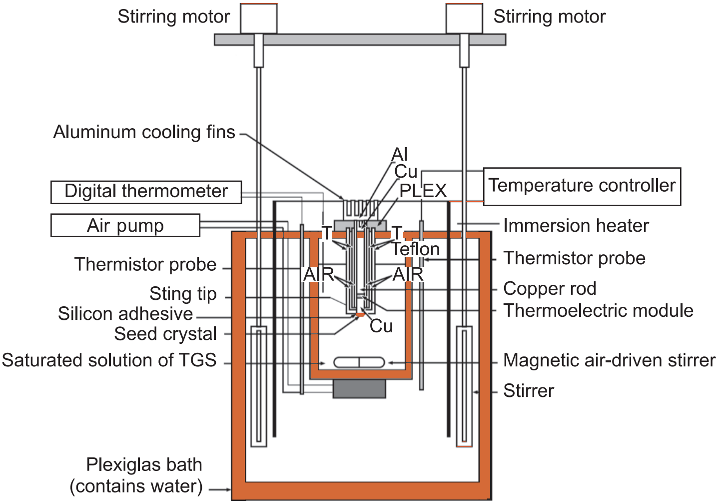
As part of the NASA Microgravity and Applications Program, a study of TGS crystal growth from solution was performed on Spacelab-3 (SL-3) and the First International Microgravity Laboratory (IML-1) missions in 1985 and 1992, respectively, where single crystals of TGS were grown from solution in microgravity conditions (10^{-6} g) for 7 days to study physical, chemical, and biological processes, i.e., biotechnology, combustion, fluid and fundamental physics, and materials science.

The microgravity environment of space provides a unique opportunity to further our understanding of various materials phenomena involving the molten, fluidic, and gaseous states by reducing or eliminating buoyancy-driven effects. Experiments in space are affected by residual microaccelerations of the spacecraft derived from atmospheric drag, reaction control systems, momentum wheels, gravity gradients, crew involvement, and other disturbances.

There is no consensus as to the microgravity level required for these experiments; in general, microgravity reduces the influence of convection, buoyancy, and sedimentation. In a low-gravity environment, convection is greatly suppressed and diffusion becomes the predominant mechanism for thermal and mass transport. Crystallization and solidification are two processes that can benefit from microgravity environment. Crystals from solution are usually grown in a closed container of limited volume. Thus, any generated convection tends to produce a circular to steady laminar convection due to buoyancy. Density differences in the fluid can arise from both temperature and concentration variations. On earth, buoyancy-driven convection may cause microscopic gas/solution inclusions and the incorporation of fluctuating dopants and other defects in the crystals. Besides degrading pyroelectric device performance, the growth yield of useful crystals is also severely affected by these defects.

Cooled Sting Technique

An alternative to the ground solution technique must be used in space; the method described here, the **cooled sting technique**, cools the seed and solution temperature at a programmed rate.



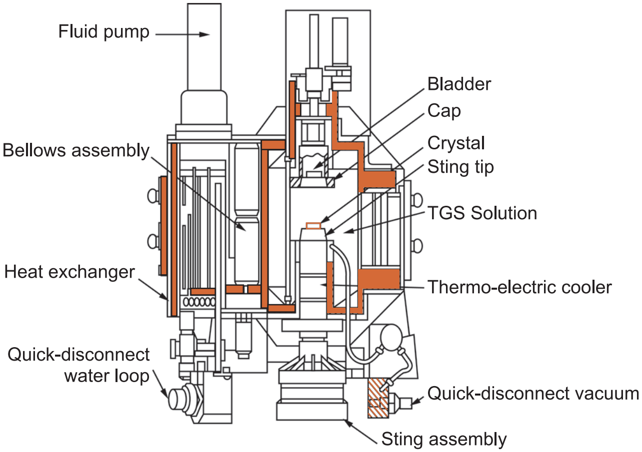
On earth, in the absence of stirring, conventional techniques of solution crystal growth lower the concentration of the solution in the vicinity of the growing crystal, resulting in an upward flow of solution. At constant temperature, this reduced concentration would rapidly lower the growth rate. In 1-g environment, most solution growth techniques increase convection mass transport by applying forced convection with very slow, programmed cooling of saturated solution. However, in the absence of convection, a change of temperature must move inward toward the crystal by conduction. The characteristic time for this to occur is

$$T = L^2 \rho Cp/k$$

where L is the distance over which the heat must be conducted, ρ is the density, Cp is the heat capacity, and k is thermal conductivity of solution. For water, it takes 48 minutes for a temperature change of 1°C to be felt at a distance of 2 cm. This is too slow to keep a constant growth rate.

Cooled Sting Technique (cont.)

The seed crystal can be programmatically cooled by using a cold finger (**sting**) in direct contact with the seed crystal, which lowers the temperature in accordance with a predetermined polynomial to maintain a supersaturated TGS solution near the surface of the crystal. Because of the L^2-dependence of T, it takes less time for a change in the sting temperature to be transmitted through the growing crystal and felt at the surface. In this case, crystals are grown by lowering the sting/seed and solution temperatures, thereby creating a desired supersaturation.



The figure illustrates the flight cell with a sting incorporated in the experimental module. The cell is designed to allow a variety of holographic diagnostics and real-time Schlieren viewing of the crystal and the surrounding fluid. Schlieren images are transmitted downlink as black-and-white video to reveal flow patterns and variation in fluid density. Holograms recorded in space give 3D information used to quantitatively determine the concentration fields surrounding the crystal and motion of particles, if present, to identify g-jitters. The modified **Fluid Experiments System** (FES) incorporates holographic tomography, which can acquire optical data through the cell at multiple angles.

Liquid Crystal Growth Methods

The techniques of growing bulk single crystals from liquid solution are generally divided into the following types:

- Growth from an aqueous/organic solution,
- Growth from silica gel,
- Hydrothermal growth,
- Growth from flux,
- High-pressure growth, and
- Growth by electrodeposition

An **aqueous/organic solution** is used to grow bulk crystals that have high solubility and vary in solubility with the change in temperature. This method generally involves seeded growth from a saturated solution. The driving force, i.e., supersaturation, is achieved by either lowering the solution temperature or evaporating the solvent. Many of the industrial processes that form crystalline products, ranging from table salt and sugar to complex pharmaceuticals, utilize this technique via spontaneous nucleation or the seeding of crystalline powders. However, the main objective of all of these processes is to obtain a high yield of small, uniform-sized crystalline products where crystalline perfection is of least importance. Such processes are not useful for growing large bulk and perfect crystals. Solution growth is the most widely used method for the growth of crystals, when the starting materials are unstable or decompose at high temperatures. This method demands that the materials must crystallize from solution with prismatic morphology.

After many modifications and refinements, the process of solution growth now yields good-quality crystals for a variety of applications. Growing crystals from solution at room temperature has many advantages over other methods, although the crystallization rate is slow. The structural imperfections in solution-grown crystals are relatively few. Low-temperature solution growth includes the slow cooling, slow evaporation, and temperature gradient methods.

Liquid–Solid Phase Transformation

The substances most suitable for crystal growth with melt techniques must melt congruently, have no polymorphous transitions, and exhibit low chemical activity.

- **Congruent melts** include the Czochralski and Bridgman–Stockbarger crystal growth methods.
- **Incongruent melts** include the top-seeded solution crystal growth method.

Congruent melting occurs during melting of a compound when the composition of the liquid that forms is the same as the composition of the solid. It can be differentiated with incongruent melting. This generally occurs in two-component systems.

The following steps occur at the start of crystal growth:

- Determination of the phase diagram,
- Material procurement,
- Selection of the temperature-controlled cylindrical furnace, and
- Selection of the crystal growth method.

Prominent liquid/solid growth methods include

- Czochralski and related techniques,
- Bridgman–Stockbarger,
- Zone melting,
- Verneuil flame fusion,
- Arc fusion growth, and
- Growth by skull melting.

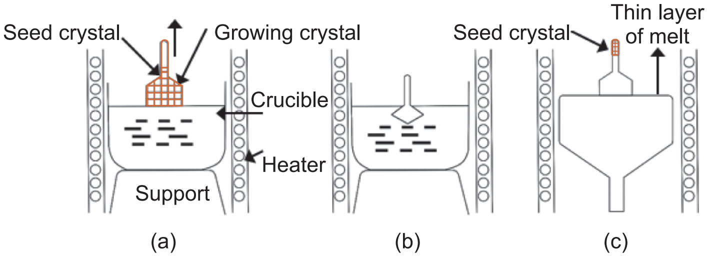
Crystal-Pulling Techniques

Crystal pulling was originally developed to measure the speed of metal crystallization. It involves the melting of a starting powder in a crucible, generally platinum, iridium, graphite, or ceramic. A rotating rod with a tiny seed crystal on the end is lowered into the crucible until it just touches the melt and then is slowly withdrawn (~1–2 mm/h). Crystallization at the interface between the melt and the seed proceeds in two ways:

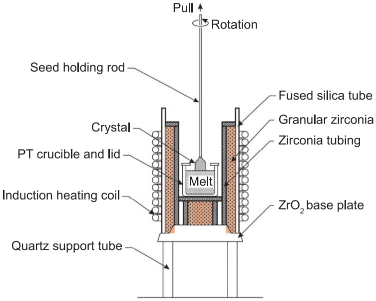
- Surface tension pulls some of the melt slightly out of the crucible onto the seed. Once this material leaves the melt, it cools just enough to solidify, adding to the seed crystal.
- Heat conduction allows the solid to extend very slightly into the melt, assuring that ample material is pulled out to make the growing crystal ever larger.

Crystal growth continues until the entire contents of the crucible have been pulled out and added to the rod. The pull rate is normally on the order of 1 mm/h to 10 cm/h.

Three techniques are shown here: (a) Czochralski (CZ), (b) Kyropoulos, and (c) pedestal. In the Kyropoulos technique, the seed is inserted into the melt but not withdrawn; instead, it is grown into it by cooling the seed via the seed holder, which acts as an effective heat leak from the furnace. In the pedestal technique, the seed is pulled from a shallow melt formed at the end of a charge rod with a larger diameter. Thus, there is no crucible.



Czochralski Technique

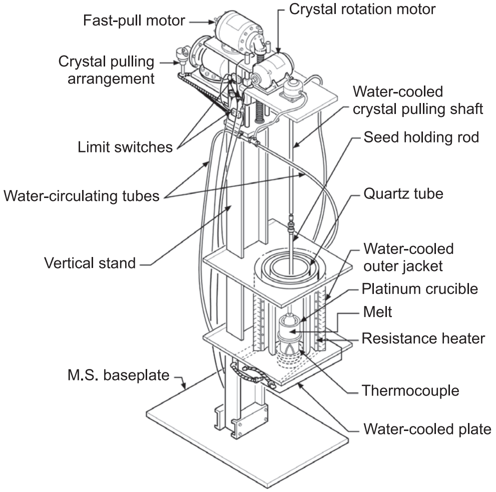


In the **Czochralski technique**, the charge is contained in a crucible that can be heated above its melting point. A pull rod with a chuck containing a seed crystal at its lower end is positioned above the crucible. The seed crystal is dipped into the melt, and its temperature is adjusted until a meniscus is supported by the seed crystal. The pull rod is then slowly lifted at an appropriate rate so that growth occurs without detachment of the seed crystal. In cases where a seed is not available, nucleation can be initiated on a twisted platinum wire. The seed is considered as a heat sink, by which the latent heat of solidification escapes, and as a nucleation center (the solidified fraction at the surface of the seed will reproduce its single-crystal structure). The seed crystal is usually rotated, and sometimes the crucible is also rotated in the counter clockwise direction to ensure symmetrical heating of the melt. These conditions normally produce grown crystals that are cylindrical in shape.

Material grown by the CZ technique can have the following properties:

- congruent melting point,
- high thermal conductivity,
- low vapor pressure,
- low viscosity,
- suitable growth habit,
- absence of easy cleavage,
- low chemical activity, and
- no solid state phase change between the melting point and room temperature.

Crystal-Pulling Apparatus



A versatile **crystal-pulling apparatus** includes the following essential features and components:

1. A rigid, vibration-free mainframe.
2. A seed crystal holder/chuck and a pull head and control of its rotation rates.
3. A range of crucibles to hold the melt that are compatible with the surrounding atmosphere.
4. Insulating materials that act as a thermal barrier around the crucible and control the thermal field in the crystallization area.
5. A heating source and temperature-control system.
6. An arrangement to control the crystal diameter.
7. A CCD camera or other optical system to view the crystal.

The furnace temperature control and crystal-weighing arrangement use a computer interface. The diameter of the growing crystal involves the melt density, solid density, and pull rate. Additional heat will decrease the diameter, and cooling will increase it.

Common Crucible Materials and Insulators

The design and choice of material for the **crucible** is critical. The chemical and physical stability of the crucible in the processing environment dictates the selection of material used to fabricate it.

Two important parameters of the crucible:

- It should not contaminate or stress the crystal.
- It should have thermal conductivity similar to that of the charge to ensure that planar isotherm profiles exist in the vicinity of the melting point of the charge.

For metals, quartz and graphite crucibles are often used. For oxide crystals, noble metals provide the best compromise between chemical stability and mechanical strength. Materials such as yttrium iron garnet, sapphire, ruby, calcium tungstate, and spinel can be pulled from iridium crucibles. Organic crystals with low melting points can be grown in glass crucibles.

Material	Maximum Operating Temperature (°C)	Melting Point (°C)
Platinum	1450	1770
Iridium	2150	2450
Alumina	1800	2015
Silica	1550	1700
Carbon	3000	—
Molybdenum	2300	2620
Tungsten	2800	3410
Graphite	3000	3652

Heating Methods for Melt Growth

The choice of the pulling atmosphere is a compromise between what is preferable for the crystal and what is preferable for the crucible, e.g., the stability of the crucible materials at the operating temperature determines the atmosphere. Common refractory materials used around the crucible are alumina-silica, pure alumina, or zirconia ceramics, depending on the operating temperature. The design of these ceramics determines the thermal gradients of the pulling process for a given crystal.

The process of heating the crucible in CZ growth systems is defined as either resistive or inductive. **Resistive heating** is used up to ∼1400°C due to the reliability, standardization, and low cost of its heating elements and power-control equipment. It can produce high uniformity of the thermal field (i.e., low thermal gradients). **Inductive heating** uses a rf generator to generate rf currents in the coil surrounding the crucible, which acts as a susceptor. The crucible must be conductive, which is the case for noble metals. If a non-conductive crucible is required, a graphite susceptor should be used that is heated so that it conducts heat to the charge in the crucible. Usually, rf generators operate in the frequency range of 10–100 kW. A 10–30-kW rf generator is suitable for general lab use and can grow crystals up to ∼30 mm in diameter.

Material and Trade Name	Maximum Operating Temperature (°C)	Permissible Atmosphere
Kanthal	1250	Oxidizing or reducing
Globar (sintered SiC)	1600	Oxidizing
Graphite	2500	Inert or vacuum
Kanthal super ($MoSi_2$)	1650	Oxidizing

Temperature Measurement and Control

Thermocouples are routinely used to measure the temperature of the melts. There are a large number of thermocouples available, ranging from chromel and alumel to Pt-Pt10%Rh and Pt-Pt13%Rh. Junctions between two thermocouple metals are produced either by fusing the two wires in a gas flame or by spot welding. Mechanical and brazed connections can also be used. Nowadays, cold junction compensation is available for all types of thermocouples in any temperature-measuring thermocouple thermometer. Basically these provide a zero suppression in accordance with the **electromagnetic field** (EMF) generated by the cold junction.

Type and Trade Name	Thermocouple Elements	Sensitivity (μV/K)	Temp. Range (°C)
Type K	Chromel, alumel	40	270–1470
Type J	Fe//$Cu_{60}Ni_{40}$	50–64	273–930
Type S	Pt/Pt10%Rh	6–11	273–1700
Type R	Pr10%Rh, Pt13%Rh	13.2	273–1760
Type C	W5%Rh, W20%Rh	—	0–2320

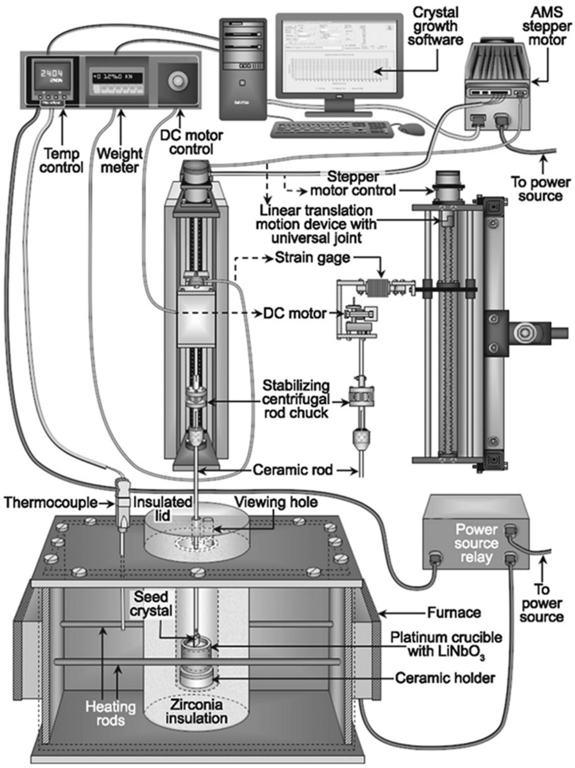
Most conventional temperature controllers, whether they are analog or microprocessor-based, are three-mode **proportional integral differential** (PID) **controllers**. Thus, the control algorithm is based on a proportional gain, an integral action, and a derivative action.

Automatic Diameter Control

Cylindrical crystals with a uniform diameter are desired by industry because of their economic advantages. **Automatic diameter-control systems** come in two types.

Optical systems use the bright meniscus ring that is formed around the crystal where it is in contact with the melt surface. Any change in the diameter of the growing crystal produces a lateral shift in the bright ring image, which changes the output signal of a detector, such as an optical pyrometer. The change in signal can be used as a feedback to appropriately correct the furnace input power.

Mechanical systems consists of a regular CZ-type pulling system that can continuously weigh the growing crystal to provide feedback to control the power and thus the temperature of the melt.



Parameters, Advantages, and Disadvantages

Pull rate: The pull rate is an accurately controlled variable because it is the velocity at which the seed crystal is pulled up.

Rotation rate: Depending on the crystal diameter and configuration, rotation rates typically range from 5 to 40 rpm.

Thermal gradients: The existence of a non-uniform temperature distribution inside and above the crucible is an absolute requisite for the crystallization process: the temperature in the liquid is obviously above the melting point T_m and those in the crystal below, the interface being at T_m.

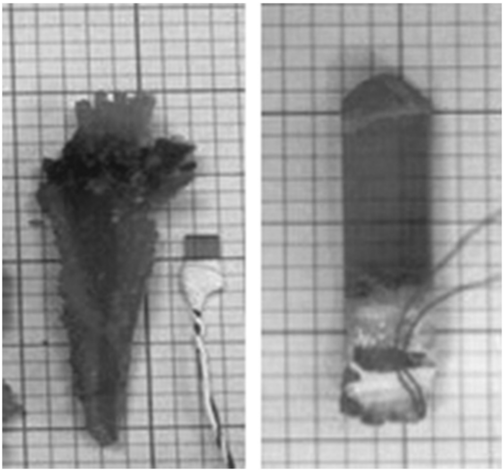
Advantages

- Growth can be achieved with a free surface (accommodates volume changes).
- The crystal can be observed.
- Forced convection is easy to impose.
- High thoughput; large crystals can be obtained.
- High crystalline perfection can be achieved.
- Good radial homogeneity.

Disadvantages

- Materials with a high vapor pressure cannot be grown.
- Batch processes are hard to adapt for continuous growth and thus produce axial segregation.
- The crystal must be rotated, and rotation of the crucible is desirable.
- The process requires continuous attention (for seeding and necking) and sophisticated control.

MNA:MAP Crystal Growth



The figure on the left shows the seed crystal along with a MNA:MAP crystal grown using the usual technique, i.e., without pulling the growing crystal. The figure on the right shows the same crystal grown with pulling, where aloe-vera-tree-type growth is avoided.

> Large crystals can be grown from a smaller amount of expensive mother liquor when the crystal is pulled while growing.

Nonlinear optical (NLO) crystals such as MNA:MAP are used to generate tunable laser beams that cover optical spectra regions by means of frequency conversion. Extensive research and development have sought to grow high-quality crystals to improve their laser performance in practical applications, i.e., extending spectral coverage into the deep-UV and mid-IR regions, including potential applications in telecommunications, THz imaging and spectroscopy, optical information processing, and optical data storage.

Recipe for Silicon Crystals

Polycrystalline silicon is placed in the crucible, and the furnace is heated above the melting point of silicon (~1420°C).

A <111>-oriented seed crystal is suspended over the crucible in the seed holder. The seed is inserted into the melt. Part of it melts, but the tip of the remaining seed crystal still touches the liquid surface. It is slowly withdrawn.

After a short duration (1–3 minutes), pulling begins at a slow rate. The new crystal will grow with a smaller diameter (slightly less than the seed diameter).

The pulling rate (mm/h) and rotation rate are increased to the final value, and the diameter of the crystal will decrease, producing a narrow neck. The length of the neck is 5–10 times the diameter of the seed.

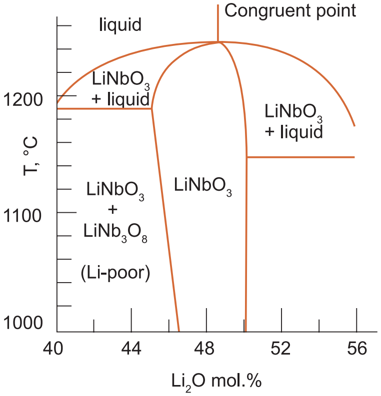
After the neck is completed, the melt temperature is slowly lowered, and the diameter of the crystal will increase. Then the melt temperature is kept constant, and the crystal attains its final diameter.

Growth at a constant diameter continues until the desired length is achieved. After that, the growth is terminated by either pulling the crystal sharply or increasing the melt temperature.

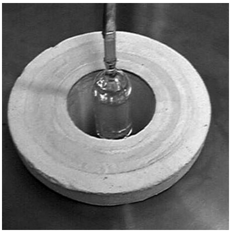
After growth is finished, the system is cooled down.

Recipe for Lithium Niobate Crystals

Lithium niobate ($LiNbO_3$, or LN) is considered one of the most important ferroelectric and photorefractive materials due to its nonlinear, electro-optic, piezoelectric, acoustical, and photorefractive properties; high electro-optic coefficient; transparency range; and the availability of large and good-quality crystals. LN is commercially grown at scale with the CZ method. Congruent LN is a well-known material that has a congruent melting point with a (Li:Nb) ratio of ~48.6:51.4 mole%, as seen in the phase diagram (Nb_2O_5-Li_2O).

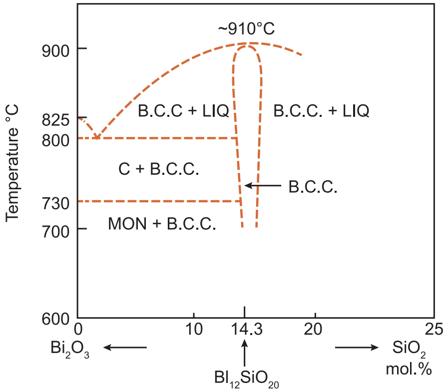


The experimental conditions for the CZ growth of LN are as follows. Nb_2O_5 and lithium carbonate can be used as the starting material, which requires a two-step sintering process: (1) heating at 700–850°C for 2–12 h to dry and calcinate carbonates and ~1150°C for 2–4 h for sintering, and (2) a grounding process at RT. Alternatively, commercial LN of the highest chemical grade enables the growth of LN crystals with excellent physical properties. Standard growth parameters include a pulling rate of 2–4 mm/h, a rotation rate of 30–40 rpm, and axial temperature gradients in the solid–liquid interface near 10°C/cm. These values are easily attainable in resistance furnaces. However, active or passive after-heaters are recommended for use with induction heaters. After terminating the growth process, the crystal is cooled 20–30°C/h, followed by fast cooling to RT. An annealing step at 1000°C for 24 h is recommended to remove strains in some cases. The LN crystal is removed from the furnance after the cooling process.



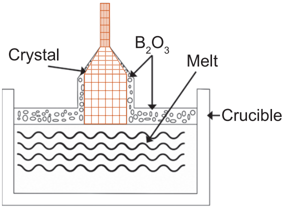
Recipe for Bismuth Silicon Oxide Crystals

Bismuth silicon oxide ($Bi_{12}SiO_{20}$, or BSO) single crystals have a variety of optical processing applications, e.g., phase-transient holography and image processing. A number of pure and Cr^{3+}-doped BSO crystals have been grown with the CZ technique and an automatic diameter-control system. Grown crystals are typically 22 mm in diameter and 65 mm in length. BSO is a cubic, photo-refractive, and electro-optic material.



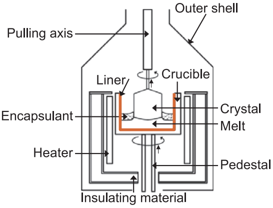
For typical BSO crystal growth, as per the phase diagram, 6 moles of 6N Johnson Matthey bismuth oxide (Bi_2O_3) and one mole of ultrapure silicon oxide (SiO_2)—or 489.25 g of Bi_2O_3 and 10.75 g of SiO_2—are thoroughly mixed and loaded in a platinum crucible 2 inches in diameter and 2 inches high. A charge of 500 g is calculated to fill the crucible to 0.5 inches below the top with molten BSO. Based on the diagram, the melting point of BSO is found to be 905°C. The charge is then melted in an induction furnace a few degrees above the melting point, and the remaining material is loaded into the hot crucible. After all of the material has been added, the charge is allowed to remain molten for 20 h. A seed crystal is slowly lowered to touch the melt surface in the thermal center of the crucible. The seed is rotated 10–20 rpm and, for best results, pulled 2 mm/h. Typical BSO crystals are 22 mm in diameter and 75 mm long, with a weight of 250–300 g.

Liquid-Encapsulated Czochralski Method



The **liquid-encapsulated Czochralski (LEC) method** is similar to the CZ method, but the crystals are grown under pressure, and the surface of the melt is covered with boron oxide (B_2O_3).

The starting materials (pre-synthesised polycrystalline chunks or, for semi-insulating GaAs, elemental Ga and As) are put in the growth crucible with a pellet of B_2O_3. The crucible is placed inside a high-pressure crystal puller and heated. At 460°C, the B_2O_3 melts to form a thick, viscous liquid that coats the entire melt, including the crucible. This layer and the pressure in the crystal puller prevent sublimation of the volatile group-V element.



The temperature is increased until the compound synthesizes (specifics vary depending on the material being produced). A seed crystal is dipped through the boron-trioxide layer into the melt. The seed is rotated and slowly withdrawn, and a single crystal propagates from the seed. Growth is monitored by CCTV, and measurements of weights, temperatures, and pressures are made at regular intervals.

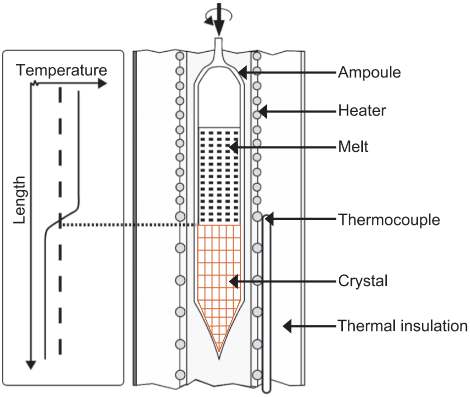
Advantages

- Materials with high vapor pressure can be grown.
- Retains most CZ advantages.
- B_2O_3 melt does not react with the crucible or ambient, but it does dissolve oxides (e.g., Ga_2O_3).

Disadvantages

- Some loss of volatile constituent.
- Contamination by B_2O_3.
- B_2O_3 is too viscous below 1000°C.
- The encapsulant is opaque near the end of growth.

Bridgman–Stockbarger Technique



Materials that melt congruently do not decompose before melting. Those that do not transform phase between the melting point and RT can be grown as a single crystal with the **Bridgman–Stockbarger** (BS) **technique**.

The material to be grown is encapsulated in a glass or quartz tube and suspended in a furnace with a suitable gradient for growth. The tip of the ampoule is conical to enhance nucleation. After the substance is melted, the ampoule is gradually moved from the hot zone to the cold zone. The lower part of the ampoule has a capillary tip in which the melt is filled; as it is lowered into the gradient, the seed initiates and gradually grows throughout the entire melt region of the ampoule. The rate at which the ampoule is lowered depends on the material, i.e., the molecular and crystalline complexity.

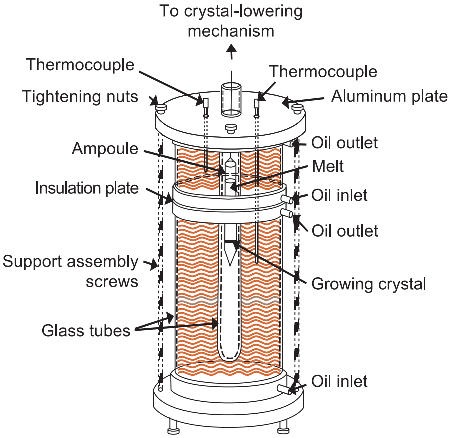
Advantages

- Radial temperature gradients are not needed to control the crystal shape.
- Low thermal stresses produce few dislocations.
- Crystals may be grown in sealed ampules (the stoichiometry of volatile melts is easy to control).
- Relatively low level of natural convection.
- Requires little attention (maintenance).

Disadvantages

- Container puts pressure on the crystal during cooling.
- Hard to observe the seeding process and the crystal.
- Level of natural convection changes as the melt is depleted. Hard to impose forced convection.
- Ampule and seed preparation, sealing, etc., do not tend toward high-throughput production.

Novel Bridgman–Stockbarger Design



The custom system shown here has two separate temperature zones, a growth chamber, ampoule-lowering arrangement, and temperature controllers. The ampoule contains 8–10 g of pure benzil $(PhCO)_2$, which can be grown at atmospheric pressure and does not need to be sealed. Prior to the start of the growth process, the ampoule is placed in the hot zone (above the melting point) of the furnace. The furnace is supported by a vertical stand that features upper and lower aluminum plates connected by 25-cm-long screws threaded on both sides. The bottom plate has screws to level the stand.

Each of the two zones has circular 10-cm-diameter tubes, ground and roughly polished on both sides, set between two machined aluminum flanges using specially molded O-ring seals and RTV two-part rubber adhesive. The hot zone is 5 cm long, and the the cold zone is ~17.5 cm. The zones are separated by a Teflon insulation plate. The centers of the insulation plate, top plate of the vertical stand, top and bottom of the upper zone, and top and bottom of the lower zone contain 2.5-cm-diameter holes through which a tube (closed at one end) is placed and sealed to the flanges using silicone O-rings. During the growth process, the ampoule is lowered through a temperature gradient as it moves through this tube from the hot zone to the cold zone. Both zones are fitted with input and output tubes connected to Neslab circulating baths that provide thermal stability to ±0.1°C. This technique can grow single crystals of benzil at a growth rate of 2.4 mm/day. The temperatures of the hot and cold zones were 97°C and 92°C, respectively.

Recipe for Bulk Lead Iodide Crystals

Since the 1970s, **lead iodide** (PbI_2) has been used for x-ray and gamma-ray detection due to its high density (6.2 g-cm^{-3}) and wide bandgap (2.3–2.5 eV), which allow detectors to operate at, or even above, room temperature. PbI_2 is similar to mercury iodide (HgI_2) with respect to its electrical properties and anisotropic (layered) structure; however, the latter undergoes a destructive phase transformation at 130°C, whereas the former is stable up to its melting point (≈410°C), has a lower vapor pressure, and can be grown directly from the melt. Growth occurs according to the following steps:

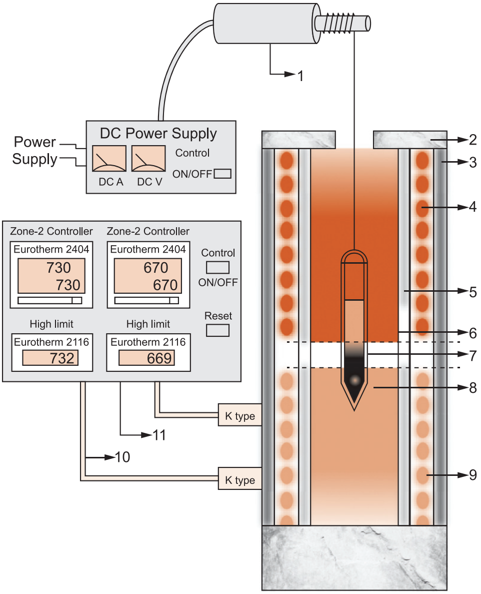
1. The polycrystalline ingot is melted in the hot region or zone 1 at $T > T_m$.
2. The melt is homogenized for a period Δt_h.
3. Crystallization begins by lowering the ampoule at a translation rate v_d (mm/h); it moves downward (relative to the furnace) along the distance Δz_B.
4. The ampoule is lowered to the end of the cold region or zone 2 at $T < T_m$.
5. The crystal is cooled while it remains at a fixed position within zone 2. Depending on the experiment, 2–3 cooling steps are performed at a cooling rate R_c, each followed by a holding period Δt_c.
6. The furnace is switched off, and the crystal cools to room temperature (20°C) by itself.

T_{Z1} (°C)	T_{Z2} (°C)	ΔT (°C)	t_R (h)	Δt_h (h)	ΔT_A (°C)	Δt_c (°C/h)	v_d (mm/h)
520	470	50	6.5	24	390	10	2

A transparent furnace allows one to observe (a) nucleation (if multiple nucleation sites occur, solidification can be restarted); (b) the melt–solid interface; (c) convection (via index of refraction changes with temperature); (d) internal temperature (tomographically with a thermal imager); and (e) crystal defects, depending on the optical properties.

Lead Iodide Setup

The two-zone transparent furnace consists of an inner quartz muffle tube surrounded by two resistive heating elements whose leads are connected externally to two Eurotherm® 2404 temperature controllers with a high-limit unit for precise control of the furnace. A gold-coated Pyrex tube surrounds the furnace to monitor the growth at higher temperatures. A DC motor lowers the quartz ampoule. The effective traveling length along the vertical axis z of the furnace is 608 mm. Hardened ceramic rings, with ceramic fiber cloth wrapped around the top and bottom of the furnace, are used to obtain a better thermal profile. During the growth process, the lower furnace opening is closed by a piece of ceramic fiber to prevent a chimney effect. Temperature control of the zones is achieved by four k-type thermocouples (T_1–T_4) placed within the windings of the resistance furnace.



(1) DC motor-lowering unit; (2) ceramic flange end plates; (3) transparent tube; (4) hot zone ($>T_m$); (5) quartz tube; (6) molten PbI_2; (7) quartz ampoule; (8) PbI_2 crystal; (9) cold zone ($<T_m$); (10) thermocouple (k-type); (11) two-zone temperature controller.

Recipe for Vanadium Pentoxide Crystals

The primary oxides of vanadium occur as a single valence in oxidation states from V^{2+} to V^{5+} in the form of VO, V_2O_3, VO_2, and finally V_2O_5, i.e., **vanadium pentoxide**, which is a saturated oxide and the most stable in the VO system. It crystallizes with an orthorhombic unit cell structure belonging to the Pmnm space group with lattice parameters $a = 11.510$ Å, $b = 3.563$ Å, and $c = 4.369$ Å with a layer-like structure.[1] In addition, V_2O_5 has a direct optical band in a visible region ($E_g = 2.2$–2.7 eV). It has relevant industrial applications in catalysts, energy-storage systems, electrochromic devices, optical switching devices, and reversible cathode materials for Li batteries.

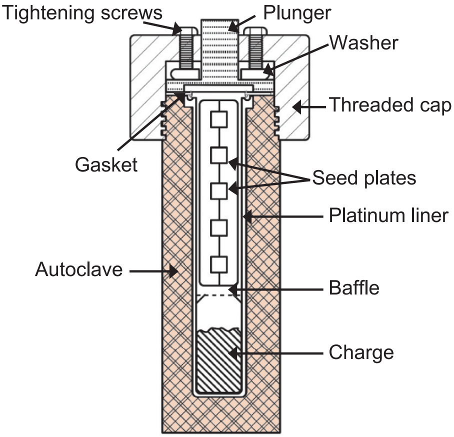
For this example, V_2O_5 powder with 99.6% purity is used as the starting material in a quartz ampoule that has a tapered or conical end to aid in grain seeding. Before starting, the ampoule should be cleaned so that there are no impurities or contamination. First, the ampoule is rinsed in water and cleaned three times with RT chemical detergent. It is then rinsed in acetone and methanol three times each at RT. Finally, the ampoule is cleaned with de-ionized water three times at RT before being dried in an oven at 95°C for 1 h. V_2O_5 weighing ~10 g is carefully loaded into the cleaned ampoule. The material is melted in the hot zone of the two-zone furnace at 679°C. The melt is left at this temperature for 24 h to ensure thermal homogeneity of the melt. A 60°C thermal gradient between the two zones and a 2-mm/h lowering rate were used to grow single crystals. For better control of the thermal gradient and to avoid thermal losses, the top and bottom of the furnace are covered with high-temperature insulation. The furnace temperature is lowered 50°C/day until 400°C, then to RT spontaneously.

This system is designed to produce high-quality semiconductor crystals. The polycrystalline material is grown into a uniform single crystal using a two-zone, transparent BS technique by controlling the growth parameters.

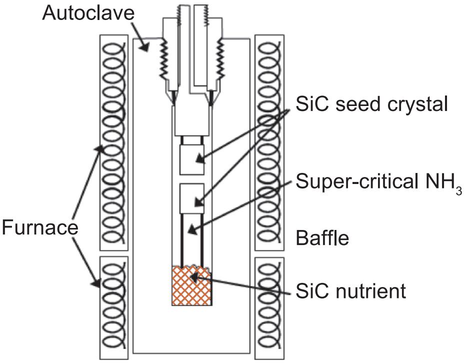
Hydrothermal Crystal Growth

Substances such as calcite and quartz are considered to be insoluble in water, but at high temperature and pressure, they are soluble. This method of crystal growth is known as the **hydrothermal method**. Temperatures typically range from 400°C to 600°C, and the pressure involved is significant (hundreds or thousands of atmospheres). Growth is usually performed in steel autoclaves with gold or silver lining. Depending on the amount of pressure, the autoclaves are categorized as low-, medium-, and high-pressure units. The concentration gradient required to produce growth is provided by a temperature difference between the nutrient and growth areas. The requirement for high pressure presents practical difficulties, and this technique only produces a few crystals of good quality and large dimensions.

Quartz is an outstanding example of industrial hydrothermal crystallization. However, one serious disadvantage of this technique is the frequent incorporation of OH ions into the crystal, which makes them unsuitable for many applications.



Ammonothermal Crystal Growth



The **ammonothermal method** is a straightforward counterpart of hydrothermal technology that is used in α-quartz crystal production. GaN-containing feedstock is dissolved in supercritical ammonia solution in one zone of the high-pressure autoclave, transported through solution by means of convection, and finally crystallized in the second zone on GaN seeds. Typical temperatures and pressures involved are 0.1–0.3 GPa and 500–900°C, respectively. The crucial point is the choice of **mineralizer**, i.e., the ionic substance added to the reaction zone to increase the reversible dissolution of GaN in ammonia.

Advantages

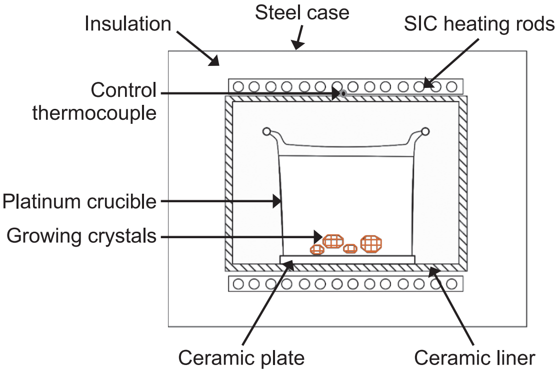
- Can grow large-diameter seeds with excellent structural properties
- Repeatable and highly controlled re-crystallization process at close-to-equilibrium conditions either by dissolution or crystallization of seeds by simple change of thermal conditions;
- Relatively low growth temperatures
- Excellent scalability of the process with the size of autoclaves.

Disadvantages

- Dissolution of nutrients into supercrital ammonia
- Transport of GaN onto the seed crystal
- Precipitation of GaN on the seed(s)

Crystal Growth from Flux

When growing crystal from **flux**, the components of the desired substance are dissolved in a solvent (flux), i.e., its melting point is lowered, in a highly stable and non-reactive crucible. To produce metallic crystals, crucibles are generally made of alumina, zirconia, and boron nitride. The crucible and its contents are often isolated from air for reaction, either by sealing them in a quartz ampoule or by using a furnace with atmospheric control. A saturated solution is prepared and kept at a temperature slightly above the saturation temperature long enough to form a complete solution. The crucible is then cooled very slowly to allow the desired material to precipitate. Crystal formation can begin by spontaneous nucleation, or it may be facilitated by a seed. Then the precipitate is separated from the flux.



This method is crucial when the material melts incongruently, undergoes a phase transition during cooling, or has very high vapor pressure at the melting point.

Flux, Crucible, and Environment

Advantages of using flux

- Readily dissolves the sample material
- Lowers the melting point to an achievable range
- High boiling point and low valor pressure
- Commercially available and minimally hazardous
- Separates from the sample material after cooling

Typical materials for flux [flux (material)]: Ga (As); Pt (B); Pb, Zn, Sn (Si, Ge, GaP, GaAs); KF ($BaTiO_3$); PbF_2 (ZnO); NaF ($MgFe_2O_4$); B_2O_3-PbO (Co_3O_4); $Na_2B_4O_7$ (Fe_2O_3); $Na_2B_4O_7$-B_2O_3 (TiO_2); and self-flux.

Advantages of using a crucible

- Very high melting point
- Does not react with the sample or flux

Typical materials for a crucible: Al_2O_3, ZrO_2, ThO_2, Pt, Ta, and Nb

Advantages of using the environment

- Very good for alloys/intermetallics
- Low stress/strain
- Good choice of flux lowers the required temperatures
- Reduced need for specialized equipment

Disadvantages of the environment

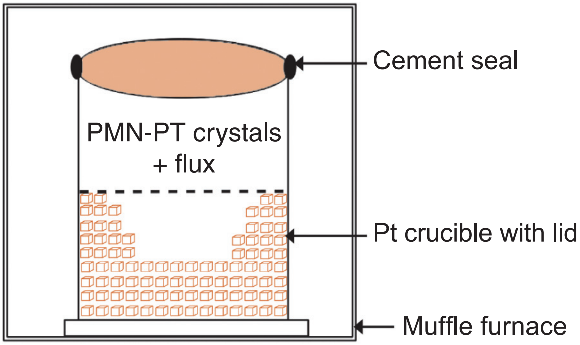
- Needs extended temperature control
- Poor nucleation control (many small crystals)
- Must find a suitable flux
- Must find a suitable crucible
- Must remove excess flux

Recipe for PMN-PT Crystals

Single crystals of **lead magnesium niobate–lead titanate** (PMN-PT) with the chemical formula $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ in the ratio 67:33 are synthesized using stoichiometric amounts of high-purity materials: PbO, MgO, Nb_2O_5, and TiO_2. The initial weight of the charge of one mole of PMN-PT solid solutions: 8.96 g of MgO, 59.10 g of Nb_2O_5, 26.63 g of TiO_2, and 223.19 g of PbO. Mix in a tumbling ball mill. Load the material in a platinum crucible covered with an alumina lid, then seal with an alumina cement. Crystal growth is performed via the gradient freeze method with either self-flux or no flux.

Temperature profile: Heating from RT to 900°C at a rate of 150°C/h and dwelling for 6 h, and then heating at 100°C/h to 1310°C and dwelling for 24 h; cooling from 1310°C to 1200°C at 2°C/h, 1200°C to 1100°C at 3°C/h, 1100°C to 800°C at 5°C/h, and 800°C to RT at 20°C/h.

Crystals form due to self-nucleation at the bottom and side of the crucible.



Growth by Electrodeposition

Electrodeposition (electrocrystallization) can apply a shiny coating of one metal on another by donating electrons to ions in a solution. This exceptionally versatile process is achieved by placing two electrodes in a solution and passing an electric current between them. The metal is then deposited at a cathode. For instance,

$$\mathrm{Zn}^{2+} + 2\mathrm{e} \rightarrow \mathrm{Zn}\,(\mathrm{solid})$$

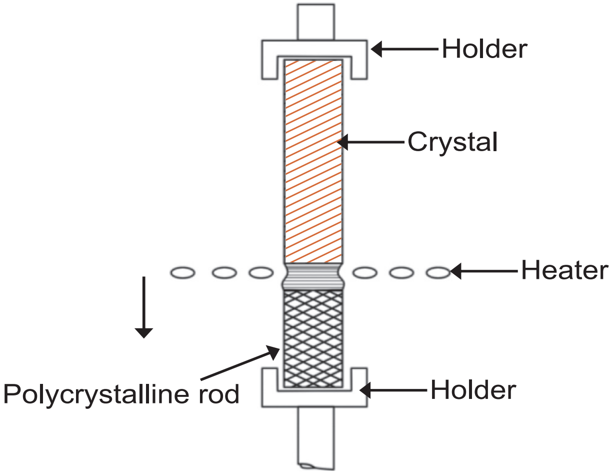
If direct current is used, then the metal is released at one of the electrodes. Crystals of Fe, W, Ag, and Ni have been grown by electrodeposition.

Two notable advantages of this process: (1) it can be controlled by changing it current density. (2) The substances can be easily separated and purified by selecting an appropriate voltage.

Electrodeposition has three main attributes that make it well suited for nano-, bio-, and microtechnologies:

- It can be used to grow functional material through complex 3D masks.
- It can be performed near room temperature from water-based electrolytes.
- It can be scaled down to the deposition of a few atoms or up to large dimensions.

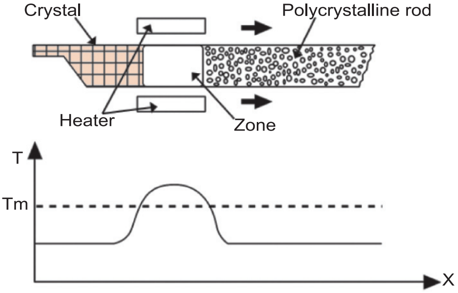
Vertical Floating Zone Melting



During the **floating zone process**, a polycrystalline crystal is translated slowly through a heater and a narrow region on crystal will be molten (floating zone). At the liquid–solid interface, the impurities diffuse from the solid region into the liquid region and segregate at the end of the ingot after the entire crystal passes through the heater. In order to grow a single crystal, a seed crystal with a certain orientation must be brought into contact with the molten region at the beginning of the process. A variety of heating systems can be used for this step, including an induction coil, resistance heater, or, more recently, an optical heating system containing high-power halogens lamps and ellipsoidal mirrors. Silicon is purified and the crystal is grown simultaneously.

Zone refining, a precursor of the floating zone technique, was first developed by W. G. Pfann in 1951 at Bell Laboratories.

Horizontal Zone Melting



In a non-conservative process, the material is added to the molten region. Only a small part of the charge is molten (except the seed). An axial temperature gradient is imposed along the crucible, and the molten zone (interface) is advanced by moving the charge or the gradient.

Advantages

- Charge is purified by repeated passage of the zone (zone refining).
- Crystals may be grown in sealed ampules or without containers (floating zone), which results in a high purity of the grown crystal.
- It can also be applied for growing single crystals of various congruently and incongruently melting materials (oxides).
- Steady-state growth is possible.
- Zone leveling is possible; can lead to superior axial homogeneity.
- Process requires little attention (maintenance).
- Simple: no need to control the shape of the crystal.
- Radial temperature gradients are high.

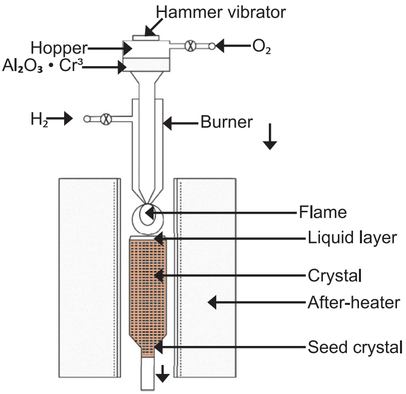
Disadvantages

- Confined growth (except in floating zone).
- Hard to observe the seeding process and the growing crystal.
- Forced convection is hard to impose (except in floating zone).
- In floating zone, materials with high vapor pressure cannot be grown.

Verneuil Flame Fusion

The **Verneuil method** (also called the **flame fusion technique**) is one of the earliest melt techniques used to grow large quantities of crystal with a high melting temperature, e.g., corundum, spinel, rutile, and strontium titanate, which are widely utilized in laser devices and precision instruments, as well as in thin technologies as substrates.

The technique utilizes a high-temperature furnace with oxygen and hydrogen supply, very fine powder (2–100 μm) source as the starting material, and a support rod with or without a seed crystal, depending on the desired crystallographic orientation of the desired crystal. During crystal growth, the source material is continuously released into the furnace chamber through a narrow tube and mixed with compressed oxygen. At the outlet of the tube, the powder is fed into an oxygen/hydrogen flame with a temperature of ~2200°C. As the powder passes through the flame, it melts into fine droplets that fall onto the support rod. A sinter one is gradually formed by the droplets and serves as a see for crystal growth. As more droplets are fed to the seed, the support rod is lowered slowly from the flame, allowing a cylindrical single crystal (a boule) to form. A typical brown boule grows up to ~100 mm in length and 15–20 mm in diameter. The cross-section of the boule is not always circular. After growth, the boule is parted lengthwise to relieve internal stress and avoid fracture.



Considerations for the Verneuil Method

Advantages

- It is technically simple, and the growth of the crystals can be observed.
- Because there is no container, there is no physicochemical interaction between the melt and the container material. Furthermore, no residual stresses result from the elastic effect of container walls.
- Crystallization can be conducted at 2000°C in air, and the oxidation and reduction potential of the crystallization atmosphere is regulated by changing the relative content of O_2 and H_2 in the flame.

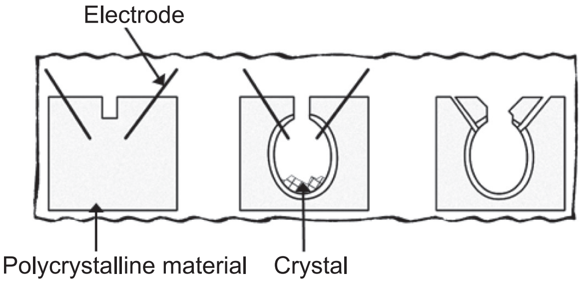
Disadvantages

- It is difficult to choose the optimal ratio of the rate at which the seed is lowered, the charge delivery, and the consumption of the delivery gas.
- Impurities can enter the melt from the working gasses.
- High temperature gradients that develop in the crystallizing zone cause high stresses.

The process was designed primarily to synthesize rubies, the first gemstones to be synthetically produced. However, the Verneuil process can also be used to produce other stones, such as sapphire, by substituting ferric oxide for chromium oxide. More elaborate stones can be created; for example, to make star sapphire, titania (titanium dioxide) is added, and the boule is kept in the heat longer, allowing needles of rutile to crystallize within it. Furthermore, crystals produced by the Verneuil process are chemically and physically equivalent to their natural counterparts, and strong magnification is usually required to distinguish between the two.

Arc Fusion Growth

Arc fusion growth involves striking an arc with graphite electrodes in a large quantity of charge material in the form of compacted powder inside a water-cooled steel enclosure. After a pool of molten material is formed due to the arc, the power is slowly reduced to stop the arc, and the melt is left to solidify. The solidified mass, which contains many crystals, is broken to harvest the crystals.



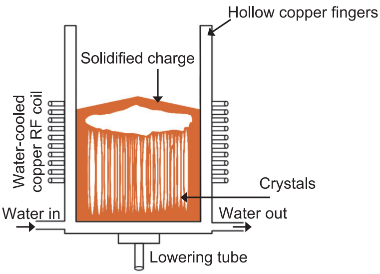
Advantages

- Because the melt is in contact with its own solid, there is no contamination from the crucible material.
- The shell left by removing the crystals can be reused by refilling it with fresh charge material, thereby economizing the process.

Disadvantages

- There is little control in this technique.
- The resulting crystals are poor in quality.

Growth by Skull Melting



The **skull-melting technique** (also called cold crucible technique) is particularly useful for growing refractory oxide crystals. In this technique, melt is kept in a solid shell (skull) with chemical composition identical to that of a melt. The melt can be held at very high temperatures (3000°C or above). The crucible is wrapped with a rf coil, which heats the charge. After the charge is melted and homogenized, crystallization is initiated either by rapid solidification or directional solidification, as in the BS technique (the former method is used for mass production).

Advantages

- In a rf system, the power can be easily controlled to one part in several thousands.
- No crucible is required, thus avoiding contamination problems or processes associated with contact between melts and hot crucibles.
- Many different types of crystals may be grown.
- Single crystals of considerable size and perfection may be grown in copious quantities.
- The stoichiometry of the materials can be controlled by using gaseous buffers to adjust the ambient environment.

Disadvantage

- A rather high initial outlay is required; however, once the system is operational, very little money is needed for maintenance, and the equipment remains operational for many years.

The Vapor Phase

Crystals can be grown from a vapor when the molecules of the gas attach themselves to a surface and create a crystal arrangement. Given a constant temperature and equilibrium conditions, the average number of molecules in the gas and solid states is constant: molecules leave the gas and attach to the surface at the same rate that they leave the surface to become gas molecules. For crystals to grow, the gas–solid chemical system must be in a non-equilibrium state such that there are too many gaseous molecules for the given pressure and temperature conditions. This state is called **supersaturation**, i.e., molecules are more prone to leave the gas and thus are deposited on the surface of the container.

Supersaturations can be induced by maintaining the crystal at a temperature lower than that of the gas. A critical stage in the growth of a crystal is seeding, whereby a small piece of crystal of the proper structure and orientation (the seed) is introduced into the growth container. The gas molecules prefer surface over the walls and preferentially deposit there. After the molecule reaches the surface of the seed, it travels across it to find a suitable site for attachment. This growth proceeds one molecule and one layer at a time. The process is slow; it takes days to grow a small crystal because the crystals are grown at temperatures well below the melting point to reduce the density of defects.

Advantage

- Crystals of high purity can be grown.

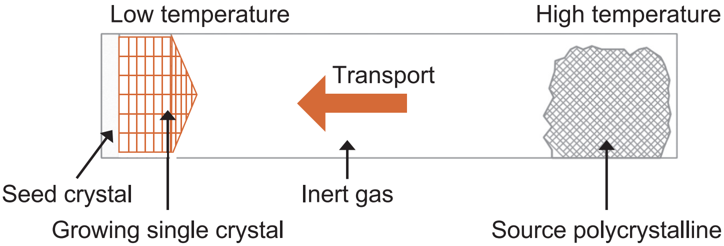
Disadvantage

- Vapor growth is a slow process.

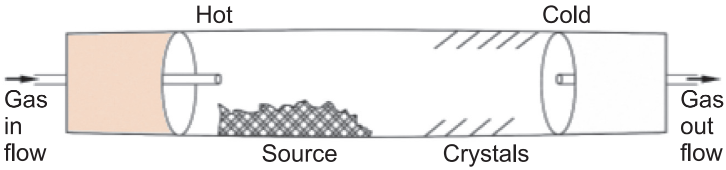
Tube-Based Systems

Vapor growth can be performed two ways.

In a **close-tube system**, the material on sublimation is transported directly, the driving force being the temperature gradient. The source material is kept at one end of the sealed tube (generally quartz) and heated to a temperature so that material sublimes. The vapor is transported to the other end of the tube, which is at lower temperature, where it condenses to form crystallites.



In an **open-tube system**, a carrier gas is additionally used to transport the growth species from the source region to the growth region. The source material is vaporized at the hot end of the tube, and an inert gas flows through the tube causing transport of vapor molecules from the higher temperature to lower temperature ide where they deposit/crystallize.



The tube can be dismounted, so it is easier to remove the grown crystals. Charge material can be introduced into the system just before the start of the growth run. This arrangement also provides control over doping at different stages and the transport rate.

Recipe for Zinc Selenide Crystals

Crystals of **zinc selenide** (ZnSe) can be created from the vapor phase as follows:

- A ZnSe seed single crystal and ZnSe polycrystalline source are sealed in a quartz ampoule.
- The crystal is grown in a low-pressure, inert gas at ~1100°C.
- The seed crystal is settled in a lower-temperature position, and the polycrystalline source material is settled in a higher-temperature region.
- The source gas sublimated from the solid source material is transported to the seed crystal according to the temperature dependence of the equilibrium constant.

The crystal is grown on the seed crystal according to the following equation:

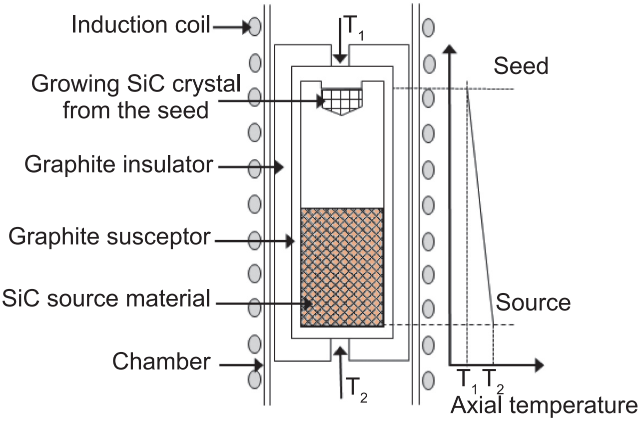
$$2\mathrm{ZnSe(solid)} \rightarrow 2\mathrm{Zn(gas)} + \mathrm{Se_2(gas)}$$

The process uses an equilibrium state so that the ZnSe crystal can be easily obtained.

The vapor growth techniques, such as PVT (physical vapor transport) and CVT (chemical vapor transport), are applied to the growth of the ZnSe single crystals. Void formation is the most important problem to be solved in the PVT growth of the ZnSe single crystal. It can be eliminated by the semi-open free-growth method, whereby the growing crystal is kept at the local minimum temperature position during growth. ZnSe single crystals 45 mm in diameter and 35 mm in length, with a dislocation density of $\sim 5 \times 10^3$ cm^{-2}, can be grown by this PVT method. A ZnSe-based white LED can be operated with a low applied voltage of 2.75 V and optical output power of 4.25 mW at a forward current of 20 mA.

Recipe for Silicon Carbide Crystals

An extraordinary combination of physical and electronic properties makes **silicon carbide** (SiC) a unique semiconductor material for devices in high-power, high-frequency, high-temperature, and intense-radiation applications.



The source material (SiC) is held at the bottom of the crucible, and the SiC seed is fixed onto the top lid of the crucible. The distance between source and seed is typically around 20 mm. The crucible is inductively heated, and operating temperatures of the system range from 1800–2600°C. A linear temperature between the source and the seed causes vapor phase transport of Si- and C-containing species from the source to the seed. The typical temperature gradient ranges from 1.0–2.5°C per mm. In most cases, the temperature at the bottom of the crystal is around 2300°C, whereas the seed temperature is around 2100°C. The crystallization process is facilitated by the supersaturation of a vapor phase species at the seed surface.

Bibliography

Aggarwal, M. D. and R. B. Lal, “Simple low-cost reciprocating crystallizer for solution crystal growth,” *Rev. Sci. Instr.* **54**, 772–773 (1983).

Aggarwal, M. D. et al., “Growth of nonlinear optical materials at Alabama A&M University,” *Proc. SPIE* **4813**, (2002) [doi: 10.1117/12.452409].

Aggarwal, M. D., J. Choi, and W. S. Wang, “Solution growth of a novel nonlinear optical material: L-Histidine tetrafluoroborate,” *J. Cryst. Growth* **204**, 179–182 (1999).

Aggarwal, M. D., J. R. Currie, B. G. Penn, A. K. Batra, and R. B. Lal, “Solution Growth and Characterization of Single Crystals on Earth and in Microgravity,” NASA Technical Memorandum TM-2007-215187, Washington, D.C. (2007).

Aggarwal, M. D., W. S. Wang, and K. Bhat, “Photonic Crystals: Crystal Growth Processing and Physical Properties,” Chapter 4 in *Handbook of Advanced Electronic and Photonic Materials and Devices*, Academic Press, New York (2001).

Batra, A. K. and M. D. Aggarwal, *Pyrolectric Materials*, SPIE Press, Bellingham, WA (2013) [doi: 10.1117/3.1000982].

Batra, A. K., M. D. Aggarwal, and R. B. Lal, “Growth and characteristics of TGS crystals grown in microgravity environment of space and on earth: an update,” in *Crystal Growth of Technologically Important Materials*, K. Byrappa, H. Klapper, T. Ohachi, and R. Fornari, Eds., Allied Publishers Pvt. Ltd., New Delhi (2003).

Batra, A. K., M. D. Aggarwal, and R. B. Lal, “Growth and characterization of doped DTGS crystals for infrared sensing devices,” *Mater. Res. Lett.* **57**, 3943–3948 (2003).

Berby, J. J. and R. A. Brown, “Thermal–capillary analysis of Czochralski and liquid encapsulated Czochralski crystal growth,” *J. Crystal Growth* **74**, 605–624 (1986).

Chernov, A. A., *Modern Crystallography III: Crystal Growth*, Springer Verlag, Berlin (1984).

Bibliography

Dhanaraj, G., K. Byrappa, V. Prasad, and M. Dudley, Eds., *Springer Handbook of Crystal Growth*, Springer, Heidelberg (2010).

Hall, J., *The Crystal Bible: A Definitive Guide to Crystals*, Godsfield Press, Hampshire, UK (2003).

Henisch, H. K., *Crystal Growth in Gels*, Dover Publications, New York (1996).

Hurle, D. T. J., *Crystal Pulling from the Melt*, Springer Verlag, London (1993).

Kaldis, E., "Crystal Growth of Electronic Materials," based on the lectures at the 5th International Summer School on Crystal Growth and Materials Research (ISSCG-5), Davos, Switzerland, (Sept. 3–10, 1983).

Lal, R. B. and M. D. Aggarwal, "Reciprocating crystallizer: Automatic crystallizer grows crystals from aqueous solutions," *NASA Tech Briefs* **8**, 419 (1984).

Lal, R. B. and A. K. Batra, "Growth and properties of triglycine sulfate (TGS): a review," *Ferroelectrics* **142**, 58–83 (1993).

Laudise, R. A., *The Growth of Single Crystals*, Prentice Hall, Englewood Cliffs, NJ (1970).

Markov, I. V., *Crystal Growth for Beginners: Fundamentals of Nucleation, Crystal Growth and Epitaxy*, 3rd edition, World Scientific Publishing Co., NJ (2016).

Mersmann, A., *Crystallization Technology Handbook*, Marcel Dekker, Inc., New York (1995).

Myersib, A. S., D. A. Green, and P. Meenan, Eds., "Crystal Growth of Organic Materials," ACS Conference Proceedings (1996).

Nicoara, D. and I. Nicoara, "An improved Bridgman-Stockbarger crystal growth system," *Mater. Sci. Eng. A* **102**, L1–L4 (1988).

Bibliography

Owens, C., K. Bhat, and W. S. Wang, "Bulk growth of high quality nonlinear optical crystals of L-Arginine tetrafluoroborate (L-AFB)," *J. Cryst. Growth* **225**, 465–469 (2001).

Sangwal, K., "On the mechanism of crystal growth from solution: An introduction," *J. Cryst. Growth* **192**, 200–214 (1998).

Scientific and Technical Information Branch, *Material Processing in Space: Earley Experiments*, National Aeronautics and Space Administration, Washington, D.C. (1980).

Scheel, H. J. and P. Capper, Eds., *Manfred Mühlberg in Crystal Growth Technology*, Wiley-VCH, Weinheim, Germany (2008).

Sloan, G. J. and A. R. McGhie, *Techniques of Melt Crystallization*, Vol. XIX of the Techniques of Chemistry series, John Wiley and Sons, New York (1971).

Surabhi, R., M. D. Aggarwal, A. K. Batra, and S. Gupta, "Design of a Low-Cost Automatic Diameter Control Czochralski (CZ) Crystal Growth System with VB.6.0 Software," *Adv. Sci. Eng. Med.* **6**(12), 1274–1279 (2014).

Index

Index

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