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 non-equilibrium 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)