

Crystal Growth History: Theory and Melt Growth Processes

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Abstract

This article gives a brief overview of the field of crystal growth over several centuries-- in fact when it wasn't a field per se, but a collection of independent scientific studies and commercial ventures undertaken by scientists and engineers from many different disciplines. This all changed after WWII with the development of semiconductor and optical devices requiring high quality single crystals. As a result, the field of crystal growth became an independent entity with societies and its own journal. What is covered here are some of the theoretical milestones along the way towards our current highly sophisticated understanding of crystallization mechanisms, crystalline perfection and some of the methods used to grow large single crystals of many different classes of materials.

Keywords

A1. Growth models, A1. Kinetic and thermodynamic factors in crystal growth, A2. Growth from melt, A2. Growth from solutions, A2. Growth from vapor, A2. Single crystal growth

Introduction

Until the invention of the transistor at Bell Laboratories shortly after WWII, research on crystals was largely curiosity driven. Studies involved understanding why both natural and laboratory created crystals formed with certain morphologies, their underlying crystal structures, the thermodynamic and kinetic behavior involved in their preparation, crystalline defects, and their formation, etc. The preceding 150 years saw many papers published on these subjects. They were conducted by physicists, chemists, metallurgists, mineralogists, and crystallographers. Crystal growth as a separate field from other scientific disciplines only started in the late 1940's and early 1950's.

The first meeting, devoted solely to the subject of crystal growth, was organized by the Faraday Society, and held in Bristol England in 1949. This first conference was attended by members of the different disciplines mentioned above in which their research activities related to the theory, growth and characterization of single crystals were discussed. Shortly thereafter, followed the publication of two books on crystal growth, one in Russian by Crystallographer A.V. Schubnikov, a compendium summarizing the studies reported in the 1949 conference, and the other written in 1951 by Buckley [1]. This latter book covered in detail, most of the crystal growth theories and methods developed up to that time.

About a decade later, (1958) a second conference on crystal growth was held in Cooperstown New York [2], following a more regional meeting two years earlier in Moscow. In 1965 a Colloquium was held in Nancy, France. From this small start, various other conferences, publications, and national and international associations devoted to crystal growth emerged.

In 1963, J.J. Gilman [3] organized and was editor of the second book devoted entirely to crystal growth and entitled, aptly, *The Art and Science of Growing Crystals*. It contained articles by various well-known scientists and engineers on both growth mechanisms, defects, and methods for the preparation of various crystals of interest at that time. The title reflects the nature of the crystal growth field, i.e., that growing a specific crystal of a new compound was largely a trial-and-error process. Over the ensuing years these scientific studies and enhanced characterization tools provided a better understanding of the underlying mechanisms involved in growing a crystal and ways to evaluate crystal quality. As a result, there was a sharp reduction in the amount of art necessary to produce crystals of a suitable size and quality necessary for various device applications. It should be pointed out since this journal issue is commemorating the 90th birthday of Alex Chernov, that in this early Gilman book, two articles, one by N.B. Cabrera and R.V. Coleman [4] and the other by W.A. Tiller (1929-2022) [5] cite some papers of Alex Chernov [6,7].

The Defining moment for the field came in 1966 with the formation of The International Organization for Crystal Growth (IOCG) and the first international conference on crystal growth (ICCG-1) held in Boston, MA. The Journal of Crystal Growth was established in 1967 under the auspices of Michael Schieber (1932-2017) and in collaboration with Sir Charles Frank (1911-1998), Bruce Chalmers (1907-1990) and Nicolás Cabrera (1913-1989). In the beginning, the idea to publish this journal was not universally accepted, but Schieber successfully persuaded some leading scientists working in the crystal growth field to convince their colleagues that this was an important venture. In 1969 the American Association for Crystal Growth was formed under the leadership of R. Laudise and K. Jackson. This was followed soon afterward by the formation of the British Association and over the next decade other national organizations sprung up in Europe, Russia, Japan, China and elsewhere. Membership in the IOCG now stands at 22 countries.

The invention of the transistor led the crystal growth field to become much more applications oriented. In this period, bulk crystals for electronic and optoelectronic applications were the main focus. Some twenty years later, around 1970, the idea of making devices from single crystal thin films on substrates of the same or different materials started to be aggressively investigated and is now a major area in the crystal growth community. In the last decade or so the emphasis has shifted to nanomaterials and complex thin film composite structures made possible by high resolution (atomic scale) characterization methods such as advanced electron, field ion and atomic force microscopes.

In brief, the crystal growth field, has three main branches 1) theoretical studies (nucleation, growth fluid dynamics and computational, etc.), 2) The growth of bulk, thin film, and fiber crystals (elements, inorganic, organic and biological materials) and 3) crystal characterization (composition, defects and physical and chemical properties). While there are many different

methods used to grow crystals, one can describe four generic types of growth processes. They are growth from 1) melts, 2) solutions, 3) vapors, and 4) by solid state recrystallization.

Applications for bulk single crystals include:

- a) Semiconductors for diodes, transistors, IC's, LED's, etc., (e.g. Si, GaAs, GaN, SiC, Hg_{1-x}Cd_xTe (MCT), and ZnO).
- b) Optical materials for windows, lenses, polarizers, laser hosts, magneto-optics, electro-optics and nonlinear devices, etc., (e.g. sapphire, CaF₂, Y₃Al₅O₁₂ (YAG), LiNbO₃, and KDP)
- c) Magnetic materials (e.g. ferrites and garnets (Y₃Fe₅O₁₂),
- d) Piezoelectric crystals (e.g. SiO₂, LiTaO₃, AlN, and xPb(Mg_{1/3}Nb_{2/3})O₃-(1-x)PbTiO₃ (PMN-PT),
- e) Pyroelectrics (e.g. Sr_xBa_{1-x}Nb₂O₆ (SBN), LiTaO₃, and PMN-025PT),
- f) Gemstones, (e.g. emerald, ruby, diamond and cubic zirconia),
- g) Radiation detectors (e.g. Eu:SrI₂, Ce: Lu_{2(1-x)}Y_{2x}SiO₅ (LYSO), and Tl:NaI) and
- h) Collimators and focusing elements (SiO₂).

While crystals can be grown by purely empirical means, enhancing growth rate, size, composition, compositional uniformity, physical properties, and crystalline perfection, etc. can be greatly facilitated by having a good grasp of the fundamentals underlying the growth processes. For most modern applications, crystal imperfections need to be either eliminated or kept to a minimum. The different types of possible defects include grain boundaries, stoichiometric variations, dislocations (line, screw, misfit), point defects (vacancies, antisite, interstitials, etc.), impurities and impurity segregation, inclusions and twins and stacking faults. The development of such an understanding of crystal growth mechanisms and defects has a long history.

Two basic disciplines are critical to crystal growth- thermodynamics (how solid, liquid and gaseous phases behave with respect to temperature, pressure and composition) and kinetics, the latter which influences our ability to produce a crystal at a desired growth rate, and with a perfection and uniformity required for an intended application

In this paper I will cover the evolution of crystal growth theory and the various methods used to grow bulk single crystals.

Evolution of crystal growth theory

From earliest times to the present day, people have been fascinated by the morphology, color, and transparency of natural crystals (see ex. Fig.1). It is clear they pondered how they were created and what led to the variety of shapes and colors these crystals came in. They wouldn't have initially known a crystal's composition, growth mechanism, atomic arrangement, and the basis of their morphology. It is not surprising, therefore, that 100's of years ago scientists began studies to unravel these mysteries and to learn to grow crystals for certain early applications. The first documented example of a commercial crystal growth factory was written up by Pliny the

Elder [8] in 77-79 AD concerning the growth of Vitriol (iron, copper, and zinc sulfates) for medicines, dyes, etc.



Figure 1. This cluster of transparent, prismatic quartz crystals containing embedded cubic bronze pyrite crystals illustrate the diversity of crystal shapes and colors found in nature. Discovering how their internal crystal structure and composition led to these different morphologies were what attracted early scientists.

According to Sunagawa (1924-2012) [9], Nicolas Steno (1638-1686) [10] was the scientist who started the science of crystal growth. Credit, however, must be also given to Conrad Gesner (1516-1565) [11] for being the first to distinguish the difference between facet angles and form in different materials. It wasn't until the 19th C, however, that a true understanding of crystal symmetry, morphology and crystalline anisotropy were quantified. In 1839, William Hallowes Miller (1801-1880) [12] came up with a scheme to describe, using symbolic representations, the orientation and direction of parallel planes (h,k,l) and directions [h,k,l] in a crystal lattice, now known as the miller indices. Almost a decade later (1848), August Bravais (1811-1853) [13] developed a more complete understanding of all the possible symmetry elements in a crystal lattice. These are known today as the Bravais lattices. There are 14 unique lattices configurations including 3 cubic, 2 tetragonal, 1 rhombohedral, 1 hexagonal, 4 orthorhombic, 2 monoclinic, and 1 triclinic. These underlying atomic forms lead to crystal faceting and shape as well as anisotropic physical and growth properties. In 1892, Fedorov and Schonflies [14,15] described the 230 space groups which define the symmetry of an object in 3 dimensions. For example, the space group of hexagonal ice is $P6_3/mmc$. The P represents a primitive cell, the 6 a sixfold symmetry down the c-axis. The first m indicates the mirror plane perpendicular to the c-axis while the second, the mirror plane parallel to that axis. The c represents glide planes.

Our understanding of the behavior of materials, was greatly advanced by J. Willard Gibbs (1839-1903) [16] who founded the field of chemical thermodynamics and whose studies led to the development of phase diagrams (based on the so-called phase rule) which are a vital source of data for crystal growers. Phase diagrams, (see example in Fig. 4 below) describe what happens to a material under various temperatures, compositions and pressures, (such as melting, decomposition, etc.) and are the equivalent to a road map describing the best parameters to employ to produce the desired crystal under the constraint of growth equipment available and regardless of its nature i.e. an element or compound. Furthermore, he showed that to form a crystal, a nutrient phase (liquid, vapor or solid must be in a metastable state, i.e., the free energy of the phase in question must exceed that of the crystal and thus provide the driving force for crystallization. This metastability can be accomplished by either supercooling or supersaturation and the amount is material dependent. The supercooling effect was first discovered by Daniel Gabriel Fahrenheit in 1724.

Of the many important contributions made by Gibbs, his work defining the energetics involved during both homogeneous and heterogeneous nucleation processes has provided the basis for our quantitative and qualitative understanding of nucleation phenomena.

In 1878 Gibbs proposed that a droplet or crystal will arrange itself such that its surface energy is minimized by assuming a shape of low surface energy,

$$\Delta G_j = \sum_j \gamma_j O_j \quad (1)$$

Where ΔG_j is the difference in energy between j molecules on the surface and inside an infinitely large crystal, γ_j = the surface Free Energy/unit area of j face and O_j is the area of the face.

Following this, the Russian crystallographer George Wulff (1863-1925) proposed in 1901 that energy minimization can be used to show that certain crystal planes are preferred over others and, therefore, can be a major factor accounting for faceting. His work resulted in the so-called Wulff plots showing that equilibrium shapes arise when $\sum A_j \gamma_j$ is minimized (where A_j is the area of the j th plane with an interfacial energy of γ_j [17]. Of course, crystal growth shape can also be strongly influenced by surface roughening conditions as well as impurities and certain processing parameters.

The 20th century led to an expansion of previous concepts on how crystals formed in different media and were instrumental in the later improvement in crystal growth technology and the development of new growth techniques. Some of these early pioneers included Harold Albert Wilson (1874-1964) [18] who around 1900 studied crystallization velocity and the viscosity of supercooled liquids and in 1909 Martin Knudsen (1871-1949) [19] developed the kinetic molecular theory which decades later led to the invention of the very important molecular beam epitaxy thin film technique (MBE). Other very important pioneers in crystal growth theory were Max Volmer (1885-1965) who together with his student Immanuel Estermann [20] proposed the adsorption layer (layer by layer) growth mechanism. Studying the vapor phase growth of Hg crystal plates, he postulated that an adsorption layer lay between a growing crystal face and the

nutrient phase, and that species are incorporated at the edges of incomplete atomic layers and growth is by the addition of ad-atoms (or molecules). This was the first solid proof of the role of surface diffusion on growth from the vapor phase. Walther Kossel (1888-1956) [21] and Iwan Stranski (1897-1979) [22] in 1928 studied the nature of chemical bonding and proposed an atomistic view of crystal growth (kinetic theory). They developed the important Kossel-Stranski TLK (terrace -ledge -kink) model an illustration of which is shown below in Figure 2.

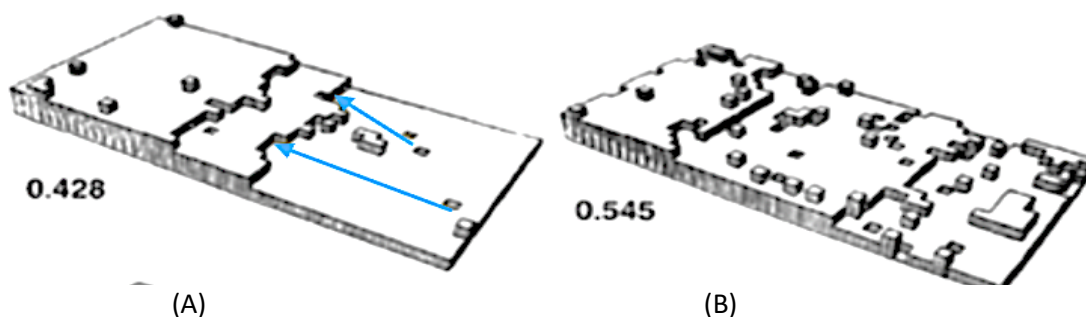


Figure 2. An illustration of the terrace-ledge-kink model of growth on a crystal surface. It shows (A) how atoms which land on a face migrate to a site with a greater number of binding sites before incorporation into the growing crystal and (B) the movement and formation of new terraces.

Rostislav Kaishev (1908-2002) together with Stranski (1897-1979) [23] formed a famous school in Bulgaria dedicated to the subject of nucleation and crystal growth, its specialty being aqueous growth the electrochemical crystallization of metals. This school also included E. Budevsky and V. Bostanov who developed the voltage impulse method to study the kinetics of 2-d nucleation on a dislocation free (100) silver electrode during electrolysis (24)

One of the most important scientists of the 20th C was Sir Charles Frank (1911-1998) [25] who, as mentioned before, was very supported of the formation of the field of crystal growth as a separate entity. He made his major scientific contribution to the area of crystalline defects, and together with W.T. Read, described the formation of line and screw dislocations in crystals and spiral surface steps. Dislocations in Si crystals, for example, were found to limit their use in electronic applications and led to techniques for their complete elimination. The invention of the transistor also led to more efforts to control crystal quality. In 1951, Burton, Cabrera and Frank [26] published on studies involving vapor phase growth on surfaces having defects such as screw dislocations, twins, etc. This led to the well-known BCF theory of layer-by-layer growth. Frank later admitted that the spiral growth model he proposed was essentially a theoretical concept and never expected to be able to observe such a structure having a molecular step height. He was unaware that Heck (27), back in 1937, had already observed spirals on paraffin crystals but didn't realize they were growth spirals. According to Chernov, Frank's idea resolved many contradictions in crystal face morphology among mineralogists, physicists and chemist on growth at low supersaturations. An excellent discussion of spiral growth and surface roughening developments since BCF was given by Bennema (28).

In 1952 Burton, Prim, and Slichter (BPS) [29] from Bell Laboratories studied how dopants and impurities were distributed along the growth direction. Within this work the concept of a boundary between the growing crystal and a melt was postulated. This boundary layer (δ), which arises due to rejection or depletion of a dopant or impurity in the interface region, can make it more difficult to get the necessary atoms or molecules to the advancing growth interface and therefore could limit the growth velocity. This is illustrated below in Figure 3.

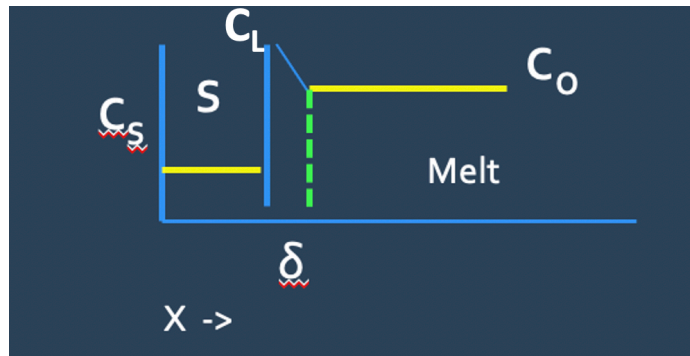


Figure 3. Schematic diagram illustrating the segregation of an impurity in a horizontally solidified melt. The initial concentration in the melt is C_o , while the amount in the solid is C_s . In the interface region a boundary layer δ forms in which the composition varies. This diagram shows the case for a segregation coefficient less than 1 as described below.

Studying how dopants and impurities are distributed along the growth direction led to the important concept of a segregation coefficient, noted as K_{eq} , in equation (2)

$$K_{eq} = C_s/C_L \quad (2)$$

where C_s is the concentration of a dopant or impurity in the solid and C_L is the concentration in the liquid at the growth interface. This equilibrium segregation coefficient can be found in the appropriate phase diagram, an example of which is illustrated below.

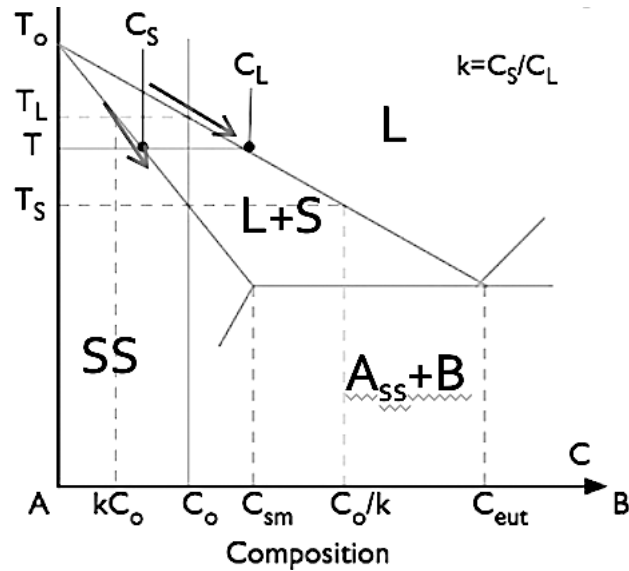


Figure 4. The solidification pathway in a hypothetical section of an A-B phase diagram with a starting melt composition of C_o . It shows how on cooling the first solid formed at T_L is equal to kC_o and has less B than the original melt. As solidification proceeds the liquid increases in B as does the crystal leading to compositional variations along a crystal until the melt reaches the eutectic composition. This diagram describes the case where $k < 1$. In cases where $k > 1$, the liquidus curve would increase with temperature.

The coefficient K can vary from a value of 1, in which case there is no segregation, and the crystal will have a uniform concentration, to values of < 1 , in which the crystal will have less solute than the melt from which it is grown leading to an enriched boundary layer, to values of > 1 where the crystal will have greater concentration of solute than the melt and a depleted boundary layer. Crystals are not normally grown under equilibrium conditions and are a growth rate dependent. Burton, Prim, and Slichter considered how growth rate affected segregation and came up with their famous “BPS” equation

$$K_{eff} = K_o / K_o + (1 - K_o) \exp(-v d / D_{solute}) \quad (3)$$

Where K_o is the equilibrium segregation coefficient, v is the freezing velocity, d is the thickness of diffusion-controlled boundary layer, and D the solute diffusion coefficient in this layer. In real practice a lot more is going on in the melt or solution, including thermal convection due to temperature gradients in a gravity field and forced convection induced by stirring via crystal and/or crucible rotation. Melt flows can reduce the thickness of the boundary layer at the freezing interface. They can also affect the interface shape (from planar to convex or concave) which in turn can affect crystal quality, including radial compositional uniformity.

The segregation behavior of melts and the need for very high purity Ge and Si for transistors led William Pfann (1917-1982) [30] at Bell Labs to develop the zone refining method. In this method unidirectional solidification was achieved by passing a small molten zone across a solid ingot whose impurities could be moved to either end of the solidified ingot (depending on whether the K_{eff} of the impurity was > 1 or < 1) and thereafter removed. While BPS theory is useful for well-

behaved systems, it does not work in all cases. A critical analysis of the limitations of the BPS theory and later modifications by various scientists was given by Carruthers [31] (from the standpoint of the mother liquor hydrodynamics) and by Chernov [32] who introduced the step kinetic coefficient for solution growth. This coefficient incorporates the solute concentration increase with step growth rate. It takes into consideration the chemical reaction rate at the kinks with the spatial characteristics of the kinks, whereas Burton, Cabrera and Frank only considered the molecular size and kink density. Their speculative conclusion was that crystal growth rate would be independent of the solvent. Chernov [32], introduced an exponential term to describe how the activation energy for attachment of a species into a kink related to the interactions of the solvent molecules with the solute and the crystal surface. The step kinetic coefficient has been used in the last 60 years to describe, predict and control the growth of ionic, organic, protein, virus, and many other classes of crystals.

Other notable contributions that should be mentioned in this brief historical overview include the work of Kenneth Jackson (1930-2022) [33]. In 1958, he published a study on surface roughening, why melt grown crystals of nonmetals had specific facets (euohedral shapes) whereas metals did not. His elegantly simple solution (given in Eq. 4) and now known as the α factor, explained and could predict experimental results.

$$\alpha = (L/KT_e) (\eta/\nu) \quad L/T_e = \Delta S_f \text{ molar entropy of fusion (4)}$$

Where L is the latent heat evolved at the interface during solidification, K is the Boltzman constant, T_e the equilibrium temperature of phase change, η is the maximum number of adatoms nearest neighbors on the surface and ν is the total number of nearest neighbor atoms in the crystal. The Jackson α factor, therefore, consists of two terms, the first being material property related (entropy of fusion divided by the gas constant) and the second a crystallographic term depending on crystal structure and surface. When α is greater than 2, you get faceted crystals, and less than 2, non-singular interfaces (dendrites). The concept of a roughening transition convincingly explained why some crystals were faceted polyhedrons and others had rounded shapes depending on whether they had atomically flat or rough interfaces, respectively.

In the case of a rough interface, typical of metals and many inorganic and organic crystals there is a gradual transition between an ordered crystal interface in contact with a disordered melt. The dependance between the linear growth rate and crystallization driving force was studied by Mikheev and Chernov (34).

In 1953, Tiller, Jackson, Rutter and Bruce Chalmers (1907-1990) [35] published on the very important topic of constitutional supercooling and segregation behavior considering the temperature gradient in a system and growth rate. The relationship they derived is given in equation (5),

$$G/R > mC_o (1/K_o-1)/D. \quad (5)$$

The left side of the equation involves the growth processing parameters G , the temperature gradient normal to the growth interface, and R , the growth rate. The right side contains material parameters including m , the slope of the liquidus curve. The net lesson of this equation is that for stable growth one needs either a steep temperature gradient or a lower growth rate. Their magnitude dependent on the material system and method under study.

In the 1950's and 1960's important contributions were also made by John W. Mullin and Robert Serkerka [36] on interfacial and morphological stability, Martin Glicksman [37] on dendritic growth and John Carruthers, Kurt Nassau [38], William Wilcox [39] and Don Hurlle [40] on the fluid dynamic behavior of melts (i.e. melt convection). The pioneering work of Robert Brown and Jeffrey Derby [41] on mathematical modelling of crystal growth processes should also be mentioned. In the last few decades developments in molecular dynamic simulations have allowed for the detailed study of interface kinetics at an atomic level which was not achievable experimentally (42).

John Cahn [43] was the first to treat anisotropic surface tension and interface attachment kinetics (for a spherical geometry) and Coriell and Serkeka [44] studied the same types of anisotropies for a planar interface. Chernov [45] treated the case of strong anisotropies. He realized that the shape of a crystal reflects the anisotropy not of the surface free energy, as per the Curie-Wulf rule, but that of the growth rate. The "Chernov rule" has become increasingly important in recent years, when better understating of the molecular mechanisms of crystallization and the roles of crystallization modifiers has allowed control of the shapes of crystals used as catalysts, pharmaceuticals, optoelectronic devices and others. In 2004, Chernov [46] discussed how interface growth kinetics has advanced during the past 50 years.

Until the early 1980's, the crystal growth community was concerned mostly with growing crystals of metals, semiconductors, inorganic, and some small molecule organic compounds. It wasn't particularly aware of efforts by researchers to grow large molecule biological materials for crystal structure analysis. However, the situation changed when NASA, planning a variety of crystal growth experiments in space, asked a few small molecule crystal growers to contribute their expertise to a major effort by pharmaceutical groups to grow biological crystals in space. To learn more about this field they organized the first international conference on protein crystal growth (later biological macromolecules) in August 1985 at Stanford University. It brought together, for the first time, both small and large molecule crystal growers to discuss the state of the current knowledge in this field and to plan new joint research programs. The result of this interaction was responsible for crystal growth scientists, such as Chernov, to begin to study the complex growth behavior of biological species. These conferences have been held tri-annually for the past 35 years.

It should be mentioned that the pharmaceutical and fine chemical industry also had a strong interest in crystallization as both a materials purification technique as well as for the preparation

of a wide range of crystalline compounds with well-controlled crystal size, shape and polymorphic form needed for optimal product performance. The processes typically involve large-scale solution growth driven by either evaporation or cooling of supersaturated solutions. The main processing goal is dissolution and stability reproducibility, thus ensuring the safety and efficacy of drug delivery systems. This community often held their industrial crystallization meetings as part of the national and international crystal growth association meetings but in addition held more specialist symposia such as national and International Symposia on Industrial Crystallization (ISIC). The British Association for Crystal Growth (BACG), in particular, has been heavily involved in this research area. An extensive review of the industrial crystallization field was provided by Horst et al. (47).

Space constraints allow for only a brief review of some of the major contributions to crystal growth theory, and unfortunately many outstanding contributions by other scientists over the past 70 years including important work on the growth of nanomaterials had to be left out. However, the research work which is discussed above had a major impact on our understanding of how crystals grow and engineers growing a wide variety of bulk and thin film crystals for device applications have benefited greatly from it.

Crystal Growth Methods

The first crystals grown by humans were probably curiosity-driven and produced by crystallization from water solutions since they could easily observe water-soluble crystals forming from evaporating ponds. Over time, new more sophisticated methods have been invented, modified, and refined so that today we have a vast arsenal of techniques from which to produce crystals of all types of materials from elemental to biological macromolecules.

The common denominator for all crystal growth methods is that they involve a phase transformation ($L \rightarrow S$, $V \rightarrow S$ and $S \rightarrow S$). The methods used to grow crystals fall into one of the following basic categories:

1. Melt growth (bulk crystals and thin film liquid phase epitaxy-LPE)
2. Solution Growth
 - Low temperature solvents
 - Aqueous
 - Organic
 - High Temperature Solvents (Flux growth)
 - Hydrothermal and Electrochemical growth
3. Vapor Growth (Bulk and thin film epitaxy-for ex. physical vapor transport (PVT), chemical vapor deposition (CVD), molecular beam epitaxy (MBE) organometallic vapor phase epitaxy, (OMVPE), etc. and

4. Solid -State Recrystallization.

The method chosen depends on the thermodynamic and kinetic properties of the material system of interest. The starting point for choosing a method depends on knowledge of the material's melting temperature, decomposition behavior, vapor pressure, etc., details of which can be obtained from a relevant phase diagram. In this paper we will only discuss bulk crystal growth methodologies.

Melt Growth

While alchemists started out trying to turn base metals into gold, they were also interested in making synthetic gemstones such as diamonds, rubies, etc. They tried various melts and, in some cases, produced small crystals. However, it was not until the beginning of the 20th C when Auguste Verneuil (1856-1913) developed the first viable commercial process for growing sizeable single crystals of very high melting temperature gemstone materials i.e., ruby and sapphire [48]. The method, called the flame fusion or Verneuil process, involves passing powder of a starting material through an oxy-hydrogen flame forming molten droplets which then fall onto a suitable substrate and solidify in atomic alignment with it.

The Czochralski (Crystal Pulling) Method

Working late one night in 1918, Jan Czochralski (1885-1953), a Polish physicist, dipped his pen, not into an ink well but into a pot of molten tin by mistake and unintentionally pulled up a single crystal rod [49]. Thus, was born our most important crystal growth method in use today. While used by only a handful of researchers in the ensuing years, it was brought out of obscurity in the early 1950's by G.K. Teal and J.B. Little [50] for the growth of the first single crystals of Ge and Si, and thus the production of superior transistors. It is still the primary method used for the commercial preparation of silicon crystals.

The Czochralski process is, in concept, very simple and involves dipping the tip of an oriented seed crystal in rod form into the surface of a melt and then withdrawing it at a rate (pull rate) such that the atoms in the melt solidify on the seed interface, thereby preserving the crystal orientation (see Fig. 5). During the process the seed is rotated to provide thermal symmetry and to stir the melt during growth. In addition to Si, crystals of a large variety of other important commercial materials, such as the semiconductors GaAs and GaP, and optoelectronic materials such as Nd: $Y_3Al_5O_{12}$ (YAG), $Gd_3Ga_5O_{12}$ (GGG), Ce: $Lu_{2(1-x)}Y_{2x}SiO_5$ (LYSO), and $LiNbO_3$, etc. can be grown by this method. Crystals of Si, for example, can reach 6 feet long and in some cases greater than 12 inches in diameter. When melts are unstable due to volatility or decomposition, high pressures and liquid encapsulation techniques have been employed. The pull rate, P, is not equivalent to the actual growth rate, G, because the melt level drops continuously during growth. As the ratio of crystal diameter to melt diameter approaches one, $G \gg P$.

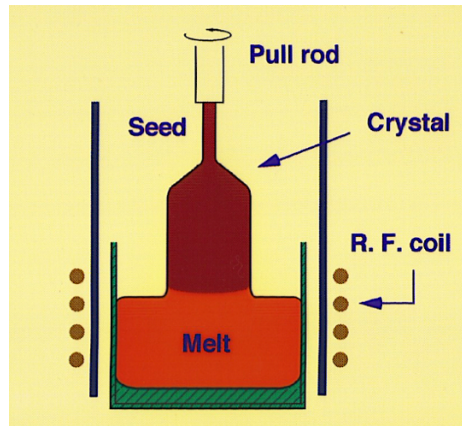


Figure 5. An illustration of the Czochralski method. The seed is both rotated and pulled up. Upon seed insertion a meniscus forms containing the solid-liquid interface. Typically, the boule is widened out slowly forming a cone to limit the rate of radial growth, but in the case of Si it can be grown out almost flat. Various heating methods can be used.

Fluid convection has been an important topic for most melt growth methods. There are two types, natural and forced convection. Natural convection results when a melt contains axial or radial thermal gradients, thus creating density differences in the melt. Forced convection is that induced with some type of stirring mechanism is used. In Czochralski growth this is accomplished by crystal rotation. Stirring can counteract density driven flows and is helpful in controlling the interface shape. In crystals with high radiative thermal conductivity, rotation can bring hot melt to the center of the interface and flatten the interface thereby reducing defects and compositional variations. In some growth processes the crucible is also rotated.

Lasers were predicted by Nobel prize winners A. Schawlow (1921-1999) and C. Townes (1915-2015) in 1958 [51]. In 1960, T. Maiman (1927-2007) [52] demonstrated the first laser using a Ruby rod. K. Nassau (1927-2010) and L. Van Uitert (1922-1999) at Bell Laboratories [53] were the first to use the Czochralski method to grow oxide crystals, the first being the laser material Nd:CaWO₄. Following that work, other important optical materials, including nonlinear compounds such as LiNbO₃ have been grown by this technique.

Many improvements have been made to the Czochralski growth method over the ensuing years, including the addition of automatic diameter control systems. Crystal or crucible weighing during growth are the most popular for commercial growth processes, but the use of lasers to monitor the actual melt meniscus position surrounding the growing crystal is also a viable technique.

The Gradient Freeze and Bridgman-Stockbarger methods.

The second most popular technique for growing crystals from the melt involves growth in ampoules in a furnace with temperature gradient. The first such technique, the gradient freeze method, was developed by Tammann (1861-1938) around 1925 [54]. He used glass tubes tapered near the bottom to control the initial nucleation of metal melts (which have a small supercooling) to the tapered region. By cooling the capillary tip, small grains formed and then by cooling the furnace the growth would proceed up the length of the tube forming a cylindrical boule with the shape of the ampoule. Also in 1925, Percy Bridgman (1882-1962) [55], working with Bi and other metals, modified Tammann's method by moving the ampoule from higher to lower temperature regions in the furnace, thereby inducing unidirectional solidification along the growth ampoule. A few years later Donald Stockbarger (1895-1961), investigating the growth of LiF and CaF and requiring better atmosphere control, modified Bridgman's technique by moving the furnace instead of the ampoule ([56,57]. The crucible design also differed between Bridgman's and Stockbarger's experiments (see Fig. 6). Bridgman used a quartz crucible with a long-tapered capillary region at the bottom for nucleation and seed selection, while Stockbarger used a crucible whose bottom had an included angle of about a 120° and rested on a cold finger used to supercool the melt locally and control the nucleation to a small number of grains. This difference was probably due to Stockbarger's need to use a non-reactive and thermally conducting crucible material with the fluoride melts. In addition, horizontal versions of these methods have also been found useful. While yielding sizeable, high quality single crystal boules at reasonable growth rates, in the early days the boules had random growth orientations.

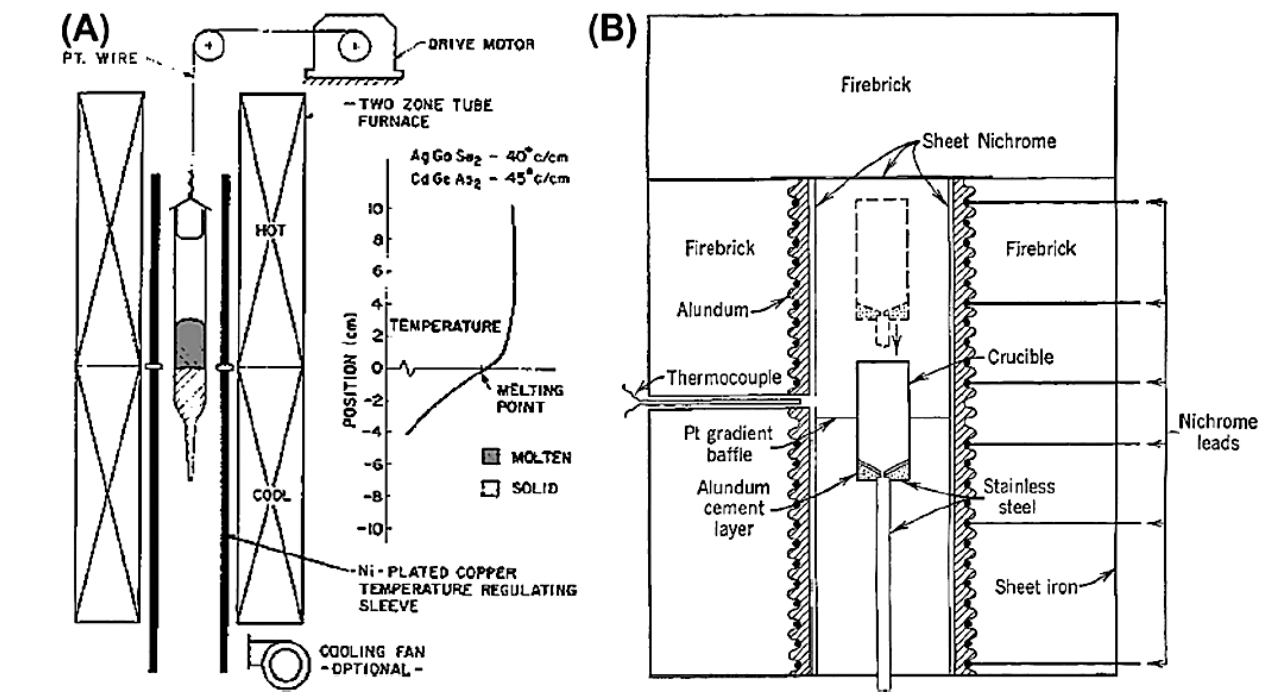


Figure 6. (A) The Bridgman method and (B) the Stockbarger technique. [1]

In subsequent years these methods underwent various modifications. One such variation involves placing an oriented seed crystal at the bottom (vertical) or end (horizontal) of the crucible. It eliminates the need to nucleate small grains which then must then fight for supremacy. Instead of the grain which is most favorably oriented with the growth axis determining the crystallographic orientation of the boule, it is the seed orientation that propagates along the growing crystal. Some of the important crystals grown by these methods include GaAs, CdTe, HgCdTe, CGeAs₂, ZnGeP₂, Tl:NaI, Pb(MgNb)TiO₃, etc.

Another variant of the gradient freeze technique is the heat exchanger method. First used by Stober [58] in 1925 for low melting materials such as NaNO₃, Zn and Bi, it was later reinvented by Schmid and Viechnicki [59] in 1970 for high melting materials. In the later version it involves locally cooling a small, oriented seed at the bottom of a large diameter flat bottom crucible and then lowering the temperature of the furnace. The seed becomes dome shaped as it grows out to fill the crucible. This commercially useful method has produced crystals of Si, sapphire, spinel, Nd:YAG and other materials in diameters of up to 30 cm.

As in the Czochralski method, control of fluid flow can enhance growth rates and improve crystal quality. This is true in other melt and solution growth processes, as well, including the Bridgeman and gradient freeze growth methods. One of most widely used is the accelerated crucible rotation growth (ACRT) method developed by H. Scheel and Dubois [60]. In this method the crucible is cyclically rotated first in one direction and then the other and centrifugal forces move the fluid relative to the crucible at the change in rotation direction. One can change the magnitude of the flows by altering the maximum rotation velocity and the time between rotation reversal. In general, well mixed melts can give more compositional uniformity and help improve growth interface shape. Other methods for controlling fluid flow include the work of Zharikov [61] in the 1980's. He introduced the idea of using a low frequency vibrating rod in the melt to induce fluid movement in Bridgman and Czochralski growth. Following that Liu et al [62] applied an acentric rotation to the Bridgman crucible and melt giving rise to a surface wave which drives flows down the outside wall of the crucible and then upward in the center from the growth interface. The tornado like melt movement at the interface was very effective at reducing the width of the boundary layer and enhancing the growth rate and compositional homogeneity.

The Kyropoulos method

In 1915, Richard Nacken (1884-1971), a prominent crystal growth researcher, developed a process for the growth of ice crystals as large as 10 cm by inserting a cold finger with an attached seed into a melt surface, thereby initiating growth [63]. The ice crystals were grown without pulling, unlike in the Czochralski method (see Fig.7a). This was the forerunner of the method developed in 1926 by Spyros Kyropoulos (1911-1967) a student of Tammann, for the growth of alkali halides crystals [64]. The Kyropoulos method was essentially an extension of Nacken's work to higher temperature systems. Instead of a seed, Kyropoulos used an air-cooled platinum rod

with a circular tip dipped into a melt (see Fig. 7B). Once some crystals were formed on the tip of the rod it was pulled up slightly to establish a stable meniscus with only one of the crystallites. The furnace was then cooled, allowing the crystallite to grow down into the melt and toward the crucible wall. This method is currently used to grow large sapphire and Tl:CsI crystals up to 30 cm in diameter. Several modifications to the method include using oriented seeds, and some initial rotation and pulling.

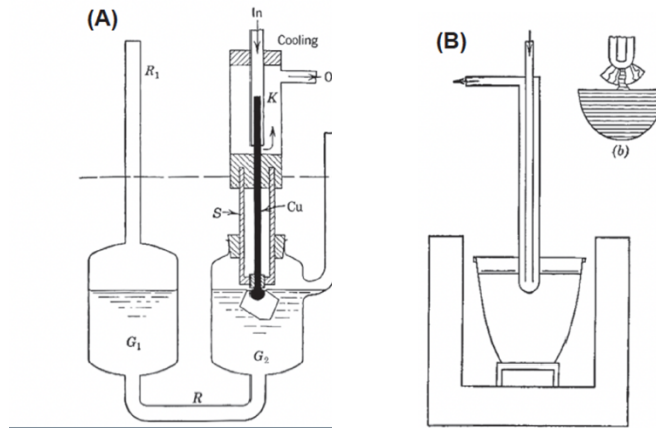


Figure 7. Comparison between the Nacken (A) and Kyropoulos (B) methods. As seen in the insert (b) in 7B, after a few grains form on the cooled rod the rod is lifted so that only one crystallite is in contact with the melt leading to a single crystal propagating upon furnace cooling. [1]

Zone Melting

Growing crystals using a small molten zone was first reported by Kapitza in 1928. In his experiments [65] he passed a small resistance heater along a tube filled with Bi producing a single crystal. This method was extended to the growth of Cd and Pb single crystals by Andrade and Roscoe [66] in 1937. Various names have been associated with this technique depending on processing differences and intent. Zone leveling, for example, is used for producing boules of uniform composition. The traveling heater method (as opposed to a moving furnace) is another. The horizontal zone refining method mentioned before, was an important use of zone melting to provide high purity semiconductor starting material for early electronic applications.

While starting melt purity was very important, it soon became apparent that melt containers could contaminate the melt during growth. For example, the oxygen contamination of Si boules grown in SiO_2 crucibles. In 1952, Henry Theuerer [67] developed the vertical float zone method in which a silicon rod containing an oriented seed crystal at one end was passed through a small heater creating a narrow moving molten zone. This so-called floating zone method was used to grow oriented single crystals of silicon for certain critical applications. Very high purity Si crystals can be grown at growth rates up to 4 mm/min. The method took on a life of its own in later years for the growth of a wide variety of materials where first non-reactive or high melting temperature crucibles could not be found, but more recently, because the development of optical heating

(lasers, xenon or halogen, lamps, etc.) provided a way to prepare single crystals with greater ease than other more conventional methods. One of these early techniques was the laser heated pedestal growth method (LHPG) [68] which allowed for the growth of single crystal fibers and small diameter rods at high growth rates and was ideal for producing samples for property evaluation as well as in the case of sapphire fibers, for device applications (see Fig.8).

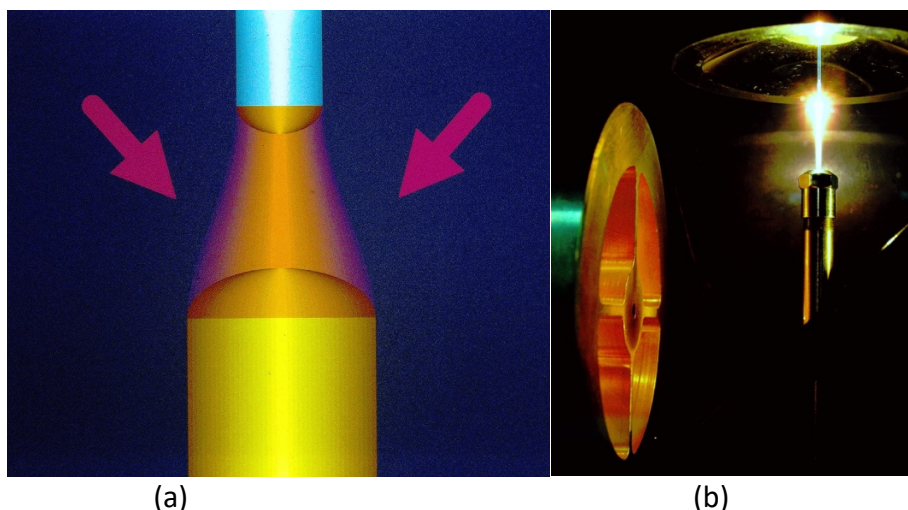


Figure 8. (a) Schematic of the pedestal float zone method. The arrows indicate the heating source, the larger diameter bottom rod is the source material and above the molten zone the growing crystal. (b) shows the laser heated pedestal growth of a sapphire fiber and the reflexicon laser optics which converts the laser beam into a circular ring around the rod.

A newer version of the zone melting technique is called the optical floating zone method [69]. It uses Xenon or halogen lamps with special optics to form circular beams. These can produce very high temperatures. It has become the favorite crystal growth method of researchers who want to produce new materials in cm-sized diameters for physical property measurements and potential device applications. Such equipment is now commercially available and so all the researcher must do is make rods of the starting material and insert them into the growth chamber. It requires minimal knowledge of crystal growth theory.

Another currently popular method for growing research grade single crystals is the micro pull down method (μ -PD). First proposed in 1980 by Mimura et al [70] but later made more widely known by the Fukuda group [71]. It uses an upper rf heated crucible holding a molten charge which is then fed through an orifice onto a seed crystal or other suitable substrate mounted on a rod. The rod is then lowered down, creating small diameter single crystals. It, like the LHPG method, has been used to prepare a large variety of doped and undoped single crystals.

Skull Melting

Another melt growth method worth mentioning is the skull melting technique developed by Wenckus [72] and Osiko [73] in the 1970's. It was meant for growing large single crystals of high melting materials without the melt contacting a crucible. The method usually involves a radio

frequency heated melt contained within a water-cooled copper coil. Initially it was used for Mn ferrites, YAG and sapphire crystals, but its principal commercial use has been for the growth of gem quality cubic zirconia ($T_{mp} = 2700^{\circ}\text{C}$).

Shaped Crystal Growth

Finally, I'd like to touch on a unique melt growth method for producing crystals having a specific, predetermined shape and that require minimal cutting and polishing for an intended application. In a limited sense the Bridgman method is a shaped growth technique since the final boule has the shape of the crucible which normally is cylindrical, but could be machined into a square, rectangular or hexagonal cross section. With an oriented seed at the bottom one could produce a boule oriented in three dimensions.

However, let us consider some other shaped growth methods. The earliest perhaps was by Von Gomperz in 1921 [74] who produced Zn and Sn fibers through a mica die. This was followed by the extensive work of Stepanov in Russia growing crystals both through wetted and non-wetted dies [75]. In the non-wetted die, the crystal has the shape of the opening in the die while in the wetted die it has the shape of the die itself. While a subset of Stepanov's method, Mlavsky and LaBelle in 1971 independently discovered the edge-defined thin film growth (EFG) method involving wetted dies [76]. It is like the Czochralski method (see Fig. 9) except that a die floats on the melt surface with an orifice to allow melt to flow up over the die surface and its outer shape determining the exterior shape of the crystal sides. One of the first applications was for sapphire tubes and plates, the former used for Na lamps and the latter used in early barcode scanner windows. A wide variety of shapes can be produced, some with great complexity. Many sapphire sheets can be growth simultaneously and are used for substrates for GaN films. Dies can be made from a variety of materials including metals, graphite, alumina, etc. One of the very important applications of shaped crystal growth technology was for the fabrications of Si sheets for lower cost solar cells. In addition to the EFG method there was the horizontal ribbon growth technique patented by Shockley in 1962, a dendrite sheet growth method, horizontal sheet casting and shaped seed techniques.

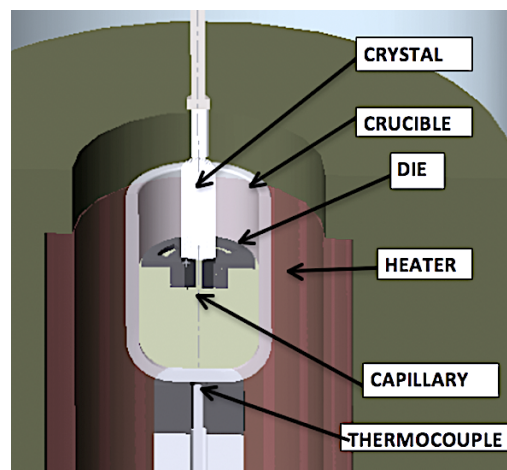


Figure 9. Schematic diagram of the EFG process containing a floating die on the melt surface. The die contains a small orifice which allows melt to flow up over the die surface by capillary action. It stops at the edges of a predetermined shape limiting the radial cross section of the crystal.

Finally, an early application for shaped crystals was the 1960 work of Ver Snyder and Guard [77] on the direct growth of Ni based super alloy single crystal turbine blades. This was like the Bridgman technique, but with a crucible in the shape of a turbine blade, At the bottom was cold plate used to control the nucleation of some melt below the blade shaped crucible. Via a complex (twisted) capillary section between the plate and crucible, a grain nucleated in the bottom melt could be directed to the main crucible leading to an oriented crystal. Single crystal turbine blades have superior creep resistance compared to polycrystalline blades.

In addition to the melt growth methods described above, there are many other variations that have been developed over the years.

Solution growth

Growing crystals from solution involves dissolving solute in a liquid, gel or melt (flux) and then recrystallizing it under controlled conditions (supersaturation, nucleation) to produce a crystal of a desired size, composition, and quality. Crystals of various materials have been produced by these methods, including small crystallites of biological materials and very large crystals of inorganic materials such as potassium dihydrogen phosphate (KDP) from aqueous solutions. Many oxide crystals have been grown from fluxes for magnetic, nonlinear and electrooptic applications. It's particularly useful for incongruently melting compounds, those that dissociate on melting, have high melting temperatures, or exhibit a high temperature phase transformation.

There are several basic generic methodologies for solution growth

1. Controlled evaporation
2. Temperature programing (usually cooling)
3. Mass transport in a concentration gradient (T_{const}), and
4. Changing the composition of the solution (salting out)

As mentioned above, Wulff's work in 1901, used aqueous solution growth techniques [17] to relate surface energy to equilibrium shape (the relationship between habit and crystal structure). Kruger and Finke [78] in 1910 were the first to investigate growth at constant temperature and supersaturation conditions. In 1949, Walker and Kolman [79], and Holman [80] at Bell Labs grew very large (40 pound) piezoelectric crystals of ethylene diamine tartrate (EDT) using seed plates and reciprocal rotation for stirring. In 1984, Rashkovich [81] first reported on the rapid growth of nonlinear optical crystals. In the ensuing years, Zaitseva et al [82] refined this rapid aqueous growth method for growing very large (800 pound) KDP crystals using unusually high supersaturations. Additionally, thermal and acoustic energy were utilized in saturated solutions to eliminate molecular clusters.

Early studies using saturated melts or fluxes to grow crystals was very popular from the 1950's until the 1990's. Initially using toxic Pb based fluxes (ex. PbO, PbF₂), researchers grew a variety of oxide crystals (ex. Y₃Fe₅O₁₂ (YIG) and similar ferrites) of varying sizes but typically on the smaller side. It was used mainly to produce crystals for physical property measurement but in some cases, for example the growth of the low temperature phase of BaB₂O₄ (β -BBO) and YIG, the crystals were large enough for device applications. In the case of β -BBO, several non Pb-based fluxes were explored, with the most commonly used being Na₂O. Crystals ~ 5 cm in diameter and 1.5 cm thick were grown by a top seeded flux growth technique. This method is similar to Czochralski growth but with much slower growth rates due to the need to transport solute through a solvent rich boundary layer to the growth interface.

Many solution growth methods involve the use of seeds to propagate large bulk crystals. However, it also has been used for producing thin films. The process is called **liquid phase epitaxy** (LPE) and has yielded very high quality epilayers using simple, inexpensive apparatus. In general, LPE films have lower point defects than materials made by other thin film techniques. Many materials have been grown in thin film form by LPE for electronic, optical, and magnetic applications. Single crystal films have been grown on substrates of the same composition (homoepitaxy), or different composition (heteroepitaxy). Perhaps, the most notable being yttrium iron garnet (YIG) for microwave and magneto-optic applications, and doped GaAs and other III-V compounds and solid solutions for light emitting diodes, lasers, solar cells and photodiodes. Various techniques have been used, including dipping the substrate into the melt through the surface, or tipping the melt from one end of a horizontal ampoule over the substrate sitting on the other end. A comprehensive treatment of flux growth method was given by Elwell and Scheel [83].

During WW II, natural crystals of α - quartz, normally obtained from Brazil, were unavailable due to German submarine activity. These high Q oscillators and filter crystals were vital for frequency control in radio transmission, submarine detection, and other electronic communications applications. It was, therefore, imperative to develop a technique to produce these crystals synthetically. At the Western Electric Corp., the **hydrothermal method** was successfully employed to grow large, high quality α - quartz crystals. This method involved growth on a rack of seed crystals immersed in a solution under high pressures and temperatures. In later years this method was applied to the growth of large crystals of ZnO for UV light emitters, spin functional devices, gas sensors, transparent electronics, and surface acoustic wave devices, as well as KTiOPO₄ (KTP) important for laser weapons, ocean optics and environmental remote sensing, etc.

In addition to the above, the **electrochemical method** can also be adapted to grow crystals from solution using either aqueous or molten salt solutions. The driving force for crystallization is the passage of a current between an anode and cathode rather than changing temperature or solution composition. The electrode can be a seed crystal, wire or more complex structure and the method can be combined with other techniques such as the crystal pulling method. It has

been used to produce various materials such as the semiconductors Si, GaP, GaAs and InP, and refractory borides phosphides, silicides and carbides. The method was first studied in 1807 by Sir Humphry Davy (1778-1829), who separated K from KOH. In 1886, it was first used for the separation of Al from Bauxite (the Hall-Heroult process). In 2005, it was used to produce well-defined nano crystals, including hexagonally shaped rods and platelets of ZnO on In-doped SnO substrates. A review of molten salt electrochemical crystal growth was given by Feigelson [84] in 1980.

Vapor phase growth

Both bulk crystals and epitaxial thin films can be grown from the vapor phase. The focus here will be on its use for bulk crystals. There are three basic techniques 1) physical vapor transport (PVT), the direct sublimation or evaporation of material followed by condensation, 2) chemical reaction transport (CRT) and 3) chemical vapor deposition (CVD). Shifts in vapor-solid equilibrium and mass transport are some of the differentiating features between these methods. Probably the first observation of a vapor growth process was made by Robert Bunsen (1811-1899). He found that Fe_2O_3 crystals were formed in volcanic gases via a reaction between FeCl_3 and water vapor. In 1861, Henri Claire-Deville (1818-1881) was the first to use a vapor growth technique to prepare oxide crystals of magnesium, titanium, and tin [85]. The first commercial vapor growth process was begun in 1880 for the fabrication of W filaments for the new incandescent lamp industry. Since then, many different types of crystals have been produced from the vapor phase, including halides, chalcogenides, oxides, pnictides and organic compounds.

In general, bulk vapor growth methods have certain advantages over other crystal growth methods in that it can be used to grow materials at temperatures lower than their melting temperature and where the material is difficult to grow because of high vapor pressure, dissociation prior to melting, etc. Vapor growth has been particularly useful for growing small crystals for physical property studies, but it is currently in use to produce large commercial sized crystals such as SiC and CdS. One downside is that growth rates tend to be slower than in melt growth. Growth can be achieved in both horizontal and vertical configurations. One of key parameters affecting crystal growth rates is the temperature gradient in the system which controls the rate of vapor transport. Several reviews on vapor growth theory and methods are available by Kaldis [86], Faktor and Garrett [87].

Physical Vapor Transport (PVT)

In the PVT method, an element or compound is vaporized from the hotter region of a furnace by congruent sublimation ($S \rightarrow V$) or evaporation ($L \rightarrow V$) and transported, to a colder region in the furnace (open or closed ampoule), where it becomes supersaturated and crystallizes on the

ampoule walls by self-nucleation or on seed crystal. In compounds, crystal stoichiometry depends on the volatility of each component. In the simplest version, a stationary furnace and ampoule is used. In 1954, Pizzarello [88] modified this method to help improve crystal size and quality. In his growth arrangement he moved the ampoule relative to the temperature gradient and thereby created a situation similar to zone melting where the source and crystal were separated by the gas phase not a melt. In 1961, Piper and Polich [89] developed a closed-tube method in which a reservoir of one component was maintained at a different temperature than the compound to control the deviation from stoichiometry. In 1955 Lely [90] reported on growing SiC crystals by sublimation. This method was further developed over the years and now is basis for the commercial production of large single crystals of SiC.

Organic crystals have also been grown by the sublimation method, one example being urea [91]. To facilitate the growth of urea a small effusion hole had to be inserted into the closed ampoule to bleed off unwanted gaseous species such as ammonia, that reduce growth rates or stop growth completely. The apparatus and a representative crystal grown in it are shown in Figure 10.

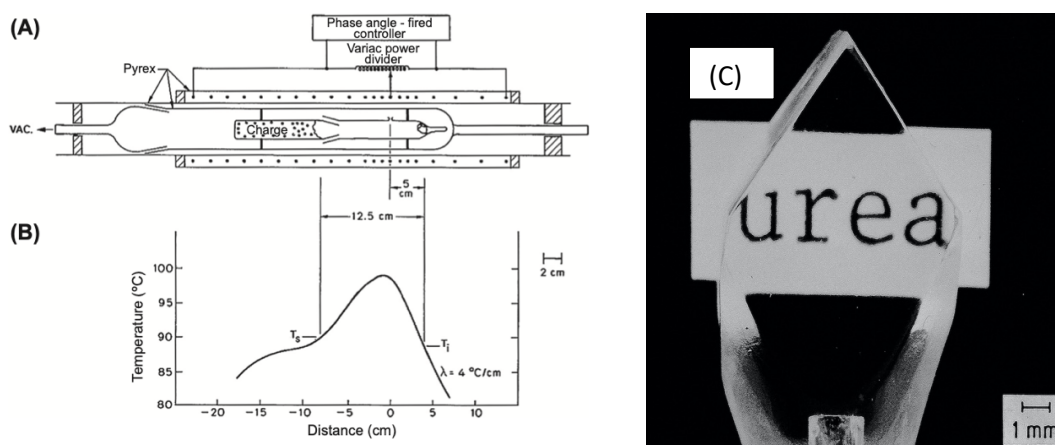


Figure 10. (A) Apparatus used to grow urea crystals by the physical vapor transport method. Note the effusion hole 5 cm from the seed, (B) the temperature profile along the growth ampoule and (C) a single crystal of urea grown by this method [90].

Chemical Reaction Transport (CVT)

For materials which have non-volatile components at convenient temperatures and pressures, a transporting agent can be employed in a closed system. The gaseous transporting agent reacts with the nonvolatile element to form a volatile complex which can then be transported to the cooler growth zone where it decomposes, leaving the element to incorporate in the growing crystal. The transporting agent then returns to the source to pick-up more of this element in a reversible process. The development of this method has been attributed to the 1925 work of Van Arkel and De Boer [92] who deposited high melting metals such as Hf and Th using I_2 as the transport agent. One example of the CVT process is the growth of ZnSe, where Zn is much less volatile than Se. Using I_2 gas in a closed ampoule system it reacts with the ZnSe source material

to form $ZnI_2(v) + Se(v)$. Together they travel to the crystal growth region where ZnSe forms and deposits on to the growing crystal, thereby releasing the I_2 to react with more ZnSe. The CVT process was comprehensively covered in the book by Harold Schäfer (1913-1992) [93].

Chemical Vapor Deposition (CVD)

The difference between the CVT and CVD methods is the latter's use of an open system and, therefore, is not reversible. While it is widely used for the epitaxial growth of semiconductor films, it is also useful for the growth of bulk crystals. One of the earliest examples of CVD growth was the work of Lorenz [94] in 1891. He grew large CdS crystals by reacting Cd(v) with H_2S gas. The growth of bulk crystals can be done in both horizontal and vertical configurations and with pressures from atmospheric to ultra-high vacuum. A wide range of materials have been grown by the CVD method including diamond, Si, III-V compounds, oxides, and nitrides. An excellent and comprehensive treatment on using the CVD method for the growth of bulk crystals was given by Schönherr [95].

Conclusion

Crystal growth has a long and colorful history starting from the earliest humans. Their curiosity and experimentation led over the centuries to the invention of methods for making current electronic, optical, and magnetic devices such as computers, lasers, and cell phones, etc. on which we rely on in our daily lives. Much of this would not have been possible without the physicists and other scientists who provided our basic understanding of the thermodynamic and kinetic principles underlying the growth processes and the development of characterization tools to study these crystals both during and after growth, allowing us to study structure and defects in great detail.

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