

Review of Structure, Properties and Fabrication of Single-Crystal Beryllium

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Abstract

Due to its unusual combination of properties, beryllium has been utilized as x-ray window material in commercial x-ray applications. Considerable interest also exists in using beryllium for synchrotron radiation optics, particularly as lenses and monochromators. High quality single-crystal beryllium may be used for these applications. For this purpose, a basic review of single-crystal beryllium is presented here, including its structure, properties and fabrication techniques. Published research from the 1950s until the present was utilized to obtain beryllium single-crystal properties and fabrication information. Studies indicate that monocrystals may be grown in any crystal orientation desired, but inadequate growth techniques have been the limiting factor in growing high quality crystals. Recent technological advancements however have finally permitted the growth of beryllium monocrystals suitable for testing as lenses and monochromators. Experiments need to be conducted to verify the feasibility of single-crystal beryllium for these applications.

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I. INTRODUCTION

Beryllium, with its low atomic number of 4, is highly transparent to energetic particles and x-rays. Coupled with a unique set of mechanical and thermal properties, it is an ideal material for use in x-ray applications. Beryllium metal windows, in the shape of disks, rectangles and arc segments, have already been extensively used in medicine and industry, for example in CT scanning, radiography, baggage inspection and other non-destructive testing

and imaging applications[1]. However, due to the inavailability of high quality beryllium crystals, the metal has not been used as an x-ray lens or monochromator, components widely employed in synchrotron light sources. To understand the details of single-crystal beryllium and its fabrication process, a basic literature review of single-crystal beryllium was required and is presented in this paper. Beryllium's properties and hazards are outlined, followed by a more detailed review of its structure and elastic properties. The paper also describes single-crystal manufacturing techniques. Fabrication processes and history of single-crystal beryllium are discussed in detail. Aspects of fracture mechanics and fatigue have been excluded however, and may be the subject of a future study.

II. ABOUT THE ADVANCED PHOTON SOURCE (SYNCHROTRON FACILITY)

The Advanced Photon Source (APS) at Argonne National Laboratory is a third generation synchrotron facility designed to provide high intensity and tunable hard x-ray beams to scientists for experimental purposes. At the APS, high energy (7-GeV) electrons move around the in a circular storage ring as a narrow, focused beam. These revolving electrons radiate intense x-rays in a broad range of frequencies. Optical elements in the facility – for example x-ray windows, lenses and monochromators – are responsible for conditioning this radiation, for example into a focused, monochromatic x-ray beam. The hard x-rays penetrate matter easily and can be used to investigate the composition, structure and function of materials of interest. The APS has provided bright x-ray beams to over 5,000 scientists from around the world and from nearly every scientific discipline, allowing the collection of valuable data that promises to impact our technologies and our understanding of the materials that make up our world[2].

III. BERYLLIUM BASICS

A. Discovery

Human beings have been in the presence of beryllium since the early days. Beryllium containing gemstones such as emerald and aquamarine have been collected and traded for countless years. French chemist Vauquelin is however credited to have first discovered the element while conducting chemical analysis on beryl[3]. He was able to obtain beryllium

hydroxide by first dissolving the beryl in aqueous alkali and then boiling the solution. The first elemental form of beryllium was extracted in 1828 in two independent experiments by German chemist Friedrich Wohler and French chemist Antoine Bussy when they reacted beryllium chloride with potassium. The gray metal produced at the end of the reaction was named beryllium by Wohler, and this name was officially adopted by IUPAC in 1957[4]. Since the early twentieth century, beryllium metal, its alloys and its oxide have been produced and used in a variety of applications.

B. Physical Properties

Beryllium is a gray metal and solid at room temperature. It has a low density, high melting and boiling points and a low coefficient of thermal expansion. The high specific heat capacity and thermal conductivity give beryllium the ability to dissipate heat very quickly. At cryogenic temperatures however, beryllium has a very low specific heat capacity. These features ensure that beryllium is thermally a very stable metal. Some principal physical properties of beryllium are outlined in Table I on page 5. Properties for aluminum, silicon and copper are also given for comparison.

Due to its low density and very high elastic modulus, beryllium has the lowest stiffness to weight ratio of all metals. The metal is classified as brittle at room temperature. Its ductility increases however at temperatures above 450 K[9], making it possible to shape the metal into the required geometry if high temperatures are maintained.

C. Chemical Properties

Beryllium is an alkaline earth metal. It has an electronic configuration of $1s^2 2s^2$, and generally exhibits a +2 oxidation state in its various compounds. The metal reacts readily with hydrochloric acid and sulphuric acid, releasing hydrogen gas and forming beryllium sulphate and beryllium chloride respectively. However, beryllium does not react with concentrated nitric acid or other oxidizing acids due to the formation of an inert layer of beryllium oxide that prevents further reaction. This inert oxide layer exists for every piece of beryllium metal that has been exposed to air, and therefore exposed beryllium only reacts with air or water at elevated temperatures[10].

Properties	Beryllium	Aluminum	Silicon	Copper
Atomic weight	9.0122	26.98	28.09	63.55
Crystal structure	hexagonal close-packed	face-centered cubic	diamond cubic	face-centered cubic
Density, g/cm ³	1.85	2.70	2.33	8.94
Melting point, °C	1287	660	1414	1084
Boiling point, °C	2469	2519	3265	2562
Latent heat of fusion, kJ/mol	12.2	10.71	50.21	13.26
Specific heat capacity, J/mol . K	16.443	24.200	19.789	24.440
Thermal conductivity, W/m . K	200	237	149	401
Electrical conductivity, [nΩ.m] ⁻¹	0.028	0.035	10 ⁻¹²	0.060
Electronegativity	1.5	1.6	1.9	1.9
Coefficient of thermal expansion, μ /K	11.3	23.1	2.6	16.5
Elastic modulus, GPa	287-318	70	185	110-128
Mohs hardness	5.5	2.75	7	3

Table I: General properties of beryllium, aluminum, silicon and copper at room temperature.[5-8]

Beryllium oxide and hydroxide are amphoteric in nature, and react with both acidic and alkaline solutions to produce beryllium salts. Beryllium reacts with strong bases to evolve hydrogen gas leaving an aqueous beryllate solution. Warm beryllium also reacts incandescently with phosphorous, chlorine and fluorine[11].

D. Nuclear Properties

Beryllium exists in many different isotopic forms, all but one of which are either unstable or occur very rarely. For this reason, beryllium is considered a mononuclidic element, with ^9Be of atomic mass 9.012182 being the only stable isotope[3]. ^9Be isotope has four protons and five neutrons in the nucleus. Curiously, it is the only monoisotopic element with an even proton number.

Beryllium has a low cross-section for neutron capture and a high cross-section for neutron scattering, making it an excellent moderating material[12]. The exact values of the cross-sections vary depending on the neutron energy and crystal quality (impurities and grain size). The dependence on neutron energy on cross section for two separate grain sizes is qualitatively shown in Figure 1 on page 7. At higher neutron energies, the total cross section is nearly identical for both coarse-grained and fine-grained beryllium.

E. Hazards and Safety Measures

Having outlined some of the general properties of beryllium, it is important to describe its associated hazards and proper safety measures required when working with this element. The toxicity of beryllium has been investigated since the 1950s, and many research articles have been published, sometimes with conflicting results.

The Occupational Safety and Health Administration (OSHA) - a federal agency of the United States that regulates workplace safety and health - categorizes beryllium metal powder and dust as a Class B poison[11]. The powder or dust is highly toxic if inhaled, and severe exposure can lead to an ailment known as chronic beryllium disease. OSHA has adopted a limit of $2 \mu\text{g}/\text{m}^3$ of beryllium dust in air as the maximum daily occupational exposure[11]. Beryllium powder is flammable and high concentrations of beryllium dust may even be explosive, producing extremely toxic fumes of beryllium oxide.

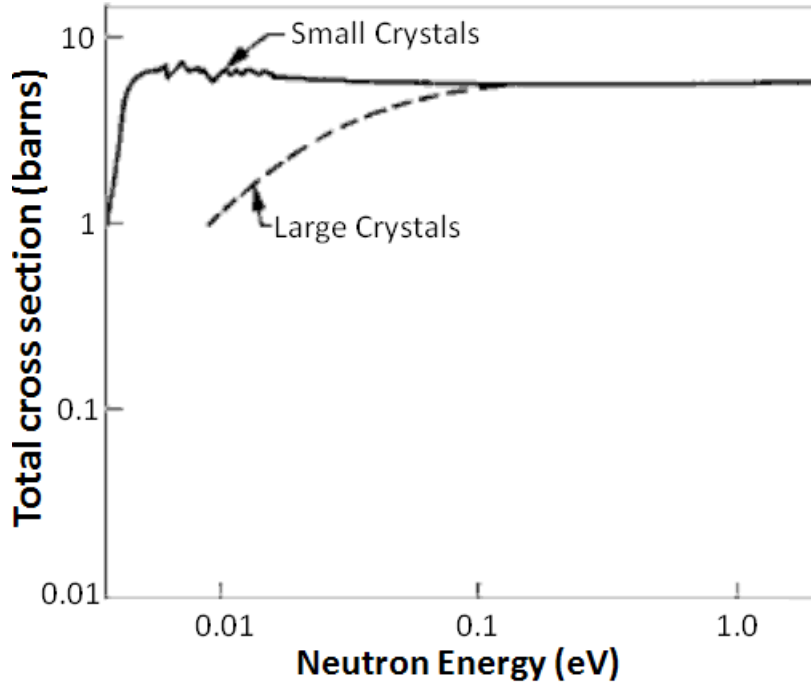


Figure 1: Total neutron cross-section as a function of neutron energy for fine-grained (small) and coarse-grained (large) beryllium.[13]

Prolonged or repeated contact of beryllium with skin can cause irritation, and may lead to dermatitis[14]. Beryllium dust or powder can irritate the eyes, producing itching, burning, or conjunctivitis[14]. There are no known harmful effects of ingesting beryllium because very small amounts are absorbed from the intestine into the bloodstream. In fact earlier scientists used to taste compounds to confirm the presence of beryllium, since beryllium compounds have a characteristic sweetness. Investigations on laboratory animals however warn against any such practice. Experiments on the animals indicate that ingesting beryllium or its compounds may lead to sarcomas and lesions[15].

The carcinogenicity of beryllium has still not been scientifically established. The International Agency for Research on Cancer (IARC) believes that beryllium and beryllium compounds are carcinogenic to both animals and humans (Group 1 carcinogens)[16]. OSHA categorizes beryllium and its compounds as a potential cancer hazard to humans[11]. Surveys on humans indicate a casual relationship between beryllium exposure and increase in cancer risk[15]. However, very recent studies suggest that once adjustment factors such as smoking are taken into account, the increase in cancer rates is statistically insignificant[17]. The new analyses suggest the reclassification of beryllium as a non-carcinogen.

Space Group	$P6_3/mmc$ (Space group number: 194)
a	2.286 Å
c	3.583 Å

Table II: beryllium hcp parameters[20]

Due to beryllium’s toxicity, certain safety precautions need to be followed in places where fabrication or machining of beryllium or its compounds takes place. Beryllium levels in the workplace need to be monitored to ensure compliance with exposure limits. Eyewash stations and safety showers should be available. Approved respirators should be provided for processes that would exceed the exposure limit, and for emergencies. High levels of fumes may be generated when beryllium metal or its alloys are heated. Such workplaces should be kept isolated and well ventilated with fresh-air. It is also essential to protect the environment by purifying the exhaust air before releasing it into the atmosphere. A detailed description of hazards and safety measures associated with beryllium may be found in the Materials Safety Data Sheet.

IV. SINGLE-CRYSTAL BERYLLIUM

A. Beryllium Crystal Structure and Properties

1. Structure

Beryllium solid exhibits two different crystal lattice structures. The more general form of beryllium is hexagonal close-packed (hcp) known as α -beryllium. At 1250°C however, beryllium bonds rearrange into a body-centered cubic (bcc) structure. This form is called β -beryllium and is stable between this transition point and beryllium’s melting temperature of 1287°C.

Figure 2a on page 9 shows a unit cell in the hcp structure. Figure 2b on page 9 shows the hexagonal symmetry in the unit cell. Due to its hexagonal symmetry, the only important parameters of the unit cell are the lengths a and c . At room temperature, beryllium has an axial ratio (c/a) of 1.568, the smallest for any hcp metal. Table II on page 8 gives more information about the crystal structure of beryllium.

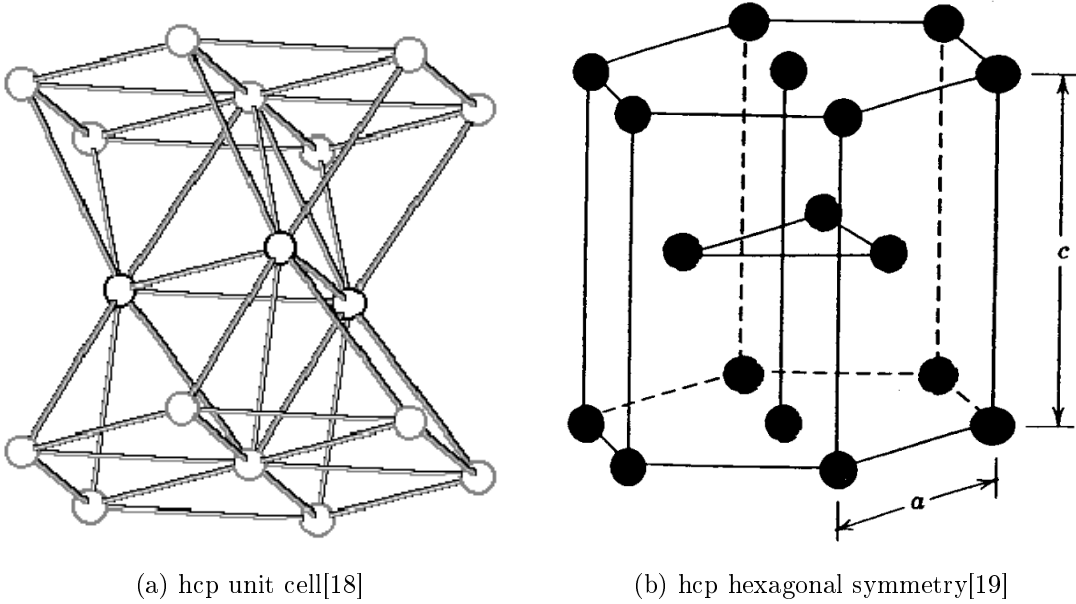


Figure 2

Scientists use beryllium’s small axial ratio to help explain the unique properties of this element.

2. Elastic Properties

The symmetries of its hcp crystal lattice make beryllium a transversely orthotropic material. This means that beryllium’s properties along the c -axis are distinct from its properties perpendicular to the c -axis (the basal plane). In orthotropic materials, only five independent parameters are needed to completely describe the elastic properties of the material. If we chose \hat{e}_3 to be the symmetry axis, Hooke’s law can be written as

$$\begin{bmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{bmatrix} = \begin{bmatrix} C_{11} & C_{12} & C_{13} & 0 & 0 & 0 \\ C_{12} & C_{11} & C_{13} & 0 & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ 0 & 0 & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & 0 \\ 0 & 0 & 0 & 0 & 0 & C_{66} \end{bmatrix} \begin{bmatrix} \epsilon_1 \\ \epsilon_2 \\ \epsilon_3 \\ \epsilon_4 \\ \epsilon_5 \\ \epsilon_6 \end{bmatrix} \quad (1)$$

$$C_{66} = \frac{1}{2} (C_{11} - C_{12})$$

or

$$[\sigma] = [C][\epsilon]$$

where $[C]$ is the stiffness tensor.

The inverse relation is expressed as

$$\begin{bmatrix} \epsilon_{11} \\ \epsilon_{22} \\ \epsilon_{33} \\ \epsilon_{23} \\ \epsilon_{31} \\ \epsilon_{12} \end{bmatrix} = \begin{bmatrix} \frac{1}{E_{11}} & -\frac{\nu_{12}}{E_{11}} & -\frac{\nu_{31}}{E_{33}} & 0 & 0 & 0 \\ -\frac{\nu_{12}}{E_{11}} & \frac{1}{E_{11}} & -\frac{\nu_{31}}{E_{33}} & 0 & 0 & 0 \\ -\frac{\nu_{13}}{E_{11}} & -\frac{\nu_{13}}{E_{11}} & \frac{1}{E_{33}} & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{1}{G_{23}} & 0 & 0 \\ 0 & 0 & 0 & 0 & \frac{1}{G_{31}} & 0 \\ 0 & 0 & 0 & 0 & 0 & \frac{1}{G_{12}} \end{bmatrix} \begin{bmatrix} \sigma_{11} \\ \sigma_{22} \\ \sigma_{33} \\ \sigma_{23} \\ \sigma_{31} \\ \sigma_{12} \end{bmatrix} \quad (2)$$

$$\frac{1}{G_{23}} = \frac{1}{G_{31}} = \frac{1}{C_{44}} \\ \frac{1}{G_{12}} = \frac{1}{C_{66}} = \frac{2(1+\nu_{12})}{E_{11}}$$

or

$$[\epsilon] = [S][\sigma]$$

where $[S]$ is the compliance tensor, and $[S] = [C]^{-1}$. In both of these tensors, there are only five independent parameters. Scientists generally measure C_{11} , C_{33} , C_{44} , C_{12} and C_{13} in experimental investigations.

In the past sixty years, many experiments have been conducted to determine these elastic constants of single-crystal beryllium. Table III on page 11 shows values for C_{ij} from all known published sources. Voigt-Reuss-Hill (VRH) averaging methods were employed to calculate quasi-isotropic Young (E), bulk (B) and shear (G) moduli and Poisson ratio (ν). These four parameters are helpful in investigating the relationship between monocrystal and polycrystal beryllium.

The paper by Kadas *et al.*[29] is a theoretical undertaking to determine the elastic properties of beryllium from first principles. The paper by Migliori *et al.*[28] is an experimental investigation to measure the elastic constants of beryllium. We will pay particular attention to these two papers. Comparing their results from Table III on page 11, we see a strong agreement between the predicted and measured values of all the constants except for

Authors	L. Gold	G. Tuer	Smith, Arbogast	Fisher, Dever	Silversmith, Averbach	Testardi, Condon	Rowland, White	Migliori <i>et al.</i>	Kadas <i>et al.</i>
C_{11}	308	282	292.3	294.0	295.4	285.8	288.8	293.6	288.2
C_{33}	357	370	336.4	357.0	356.1	342.8	354.2	356.7	365.2
C_{44}	110	135	162.5	163.0	170.6	166.9	154.9	162.2	156.7
C_{66}	183	131	132.8	133.4	134.8	135.2	134.4	133.4	131.4
C_{12}	-58	20	26.7	27.6	25.9	14.8	201.0	26.8	25.4
C_{13}	87	6.6	14.0	14.2	-1.0	11.0	4.7	14.0	0.0
E	293.9	294.4	311.1	315.8	317.6	311.1	306.9	315.2	309.2
B	128	111	114.4	117.1	110.4	109.4	109.8	116.8	111.7
G	132	139	148.6	150.3	155.6	151.6	148.4	150.1	148.8
ν	0.116	0.056	0.047	0.051	0.021	0.026	0.034	0.050	0.039

Table III: Elastic constants of single-crystal beryllium at room temperature. All units are in GPa except for ν which is unit-less.[21–29]

E_{11}	E_{33}	ν_{12}	ν_{13}	ν_{31}
290.7	355.5	0.0894	0.0357	0.0437

Table IV: Principal Young moduli E_{ii} , and principal Poisson ratios ν_{ij} of beryllium.[28]

Authors	C_{33}/C_{11}	C_{44}/C_{66}
Smith, Arbogast	1.15	1.22
Fisher, Dever	1.21	1.22
Silversmith, Averbach	1.21	1.27
Testardi, Condon	1.20	1.23
Rowland, White	1.23	1.15
Migliori <i>et al.</i>	1.21	1.22
Kadas <i>et al.</i>	1.27	1.19
Average^a	1.21	1.22

^aResults from Gold[21] and Tuer[22] were not included in this table due to the significant deviation of their stiffness values from later experiments.

Table V: Measure of elastic anisotropy of single-crystal beryllium at room temperature.

C_{13} . Measurements were also made on polycrystal beryllium and excellent agreement was reported between the measured moduli values and the VRH approximated figures[28].

For readers of this paper who are not particularly familiar with the stiffness tensor, a more intuitive way to describe the elastic properties of the structure would be to provide five independent elastic constants from among the the Young, bulk and shear moduli and Poisson ratios. Table IV on page 12 gives Young moduli and Poisson ratios for the principal directions.

A good way of measuring the degree of elastic anisotropy of hcp metals is by evaluating the ratios C_{33}/C_{11} , C_{44}/C_{66} and C_{12}/C_{13} . A value of unity for all three indicates perfect isotropy. We calculated the C_{33}/C_{11} and C_{44}/C_{66} ratios for beryllium from published data. Values for C_{12}/C_{13} were not calculated due to the high discrepancy in the measured values. The results are given in Table V on page 12. With an average of 1.21 for C_{33}/C_{11} and 1.22 for C_{44}/C_{66} , beryllium is seen to exhibit some anisotropic behavior.

So far, we have only considered the properties of beryllium at room temperature. We will now outline the effect of changing temperature on some of these important properties.

As mentioned earlier, the hexagonal axial ratio (c/a) for beryllium at room temperature is 1.568. However, this ratio varies with changing temperature. Figure 3a on page 14 shows this variation as suggested by a theoretical model. Figure 3b on page 14 shows this variation as measured in an experiment.

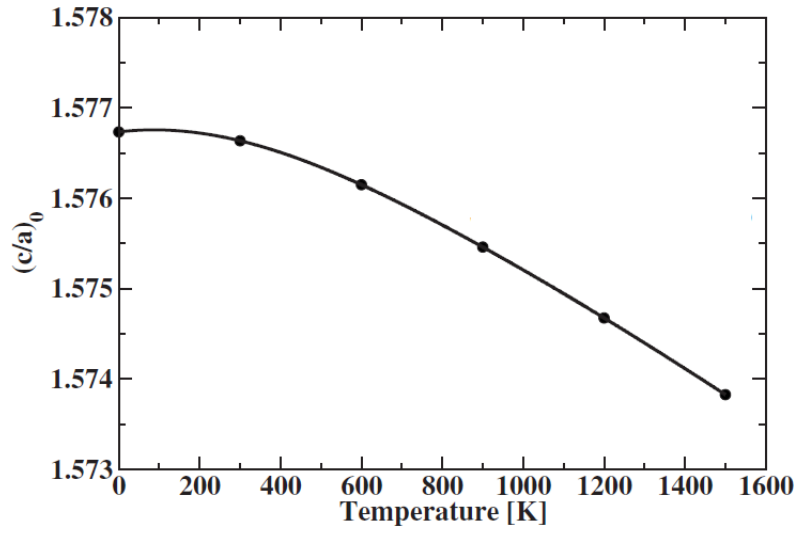
Using values from the graph, we estimate that the axial ratio decreases by not more than 0.4% for either of the plots. Since this change is very small, we can assume that the coefficient of thermal expansion along the a -axis is essentially equal to the thermal expansion coefficient along the c -axis at all temperatures. These results have been experimentally confirmed as well[30, 31], as shown in Figure 4 on page 15. In practical terms, this means that beryllium contracts or expands nearly isotropically with changing temperature.

The stiffness constants C_{ij} also vary with changing temperature. Figure 5 on page 15 shows their dependence on temperature. The plotted data is from three different published sources. From the graph, we see that the variation is gradual and the largest change occurs for C_{11} and C_{33} in the given temperature range. There is substantial deviation in the values from the three sources. Also, accurate data for elevated temperatures is not available. Further experiments and theoretical investigations are needed in order to more accurately ascertain the significance of changing temperature on the elastic constants of beryllium.

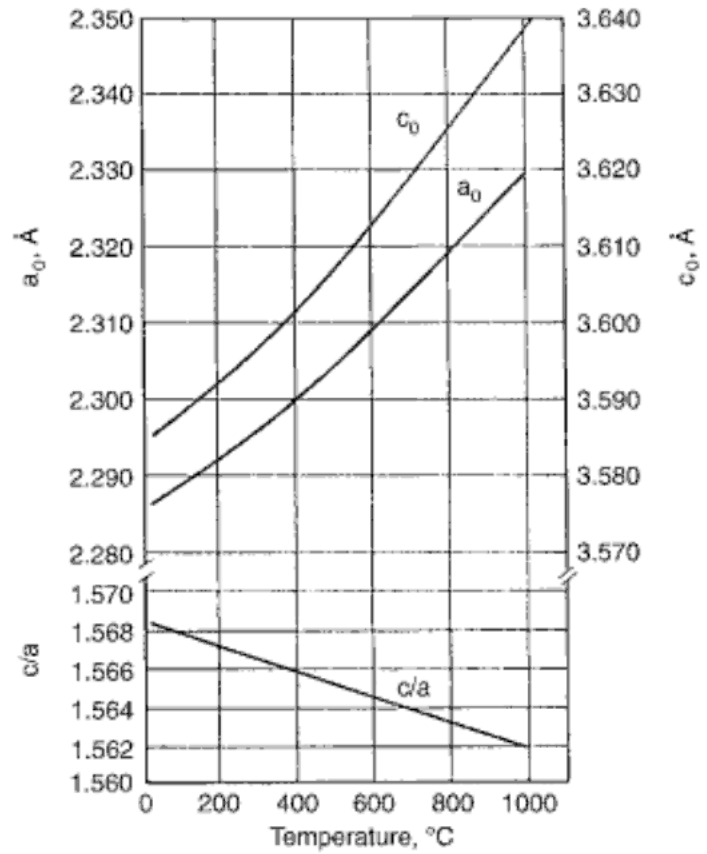
B. Manufacturing of Single-Crystals

Single crystals are employed in a variety of industrial applications that make use of their unique properties. For example large silicon monocrystals are used in semiconductor electronics for their electronic properties, whereas the high strength of single-crystal superalloys is important in turbine blades[32].

There are a number of ways of manufacturing single-crystals. However, the quality, purity and defect structure of the single-crystal product will depend on the both the material and the method used. Listed below are some of the more widely used single-crystal manufacturing techniques, along with a brief description of the apparatus and the processes involved.



(a) Theoretical unit cell axial ratio of α -beryllium as a function of temperature.[29]



(b) Measured unit cell axial ratio of α -beryllium as a function of temperature.[30]

Figure 3

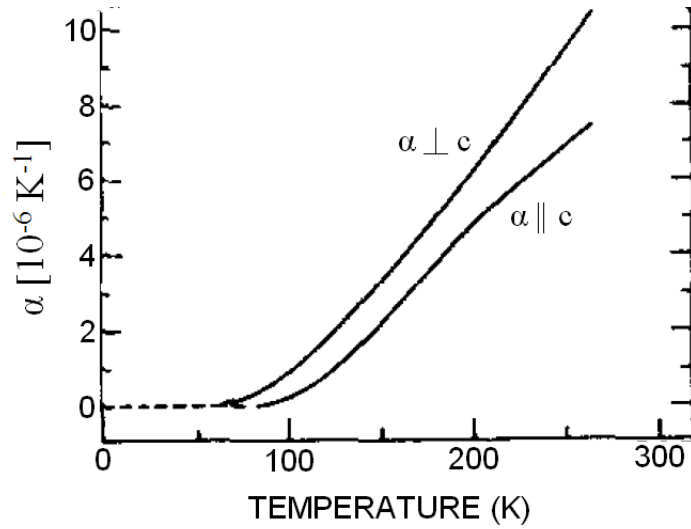


Figure 4: Measured linear thermal expansion coefficients as a function of temperature.[30]

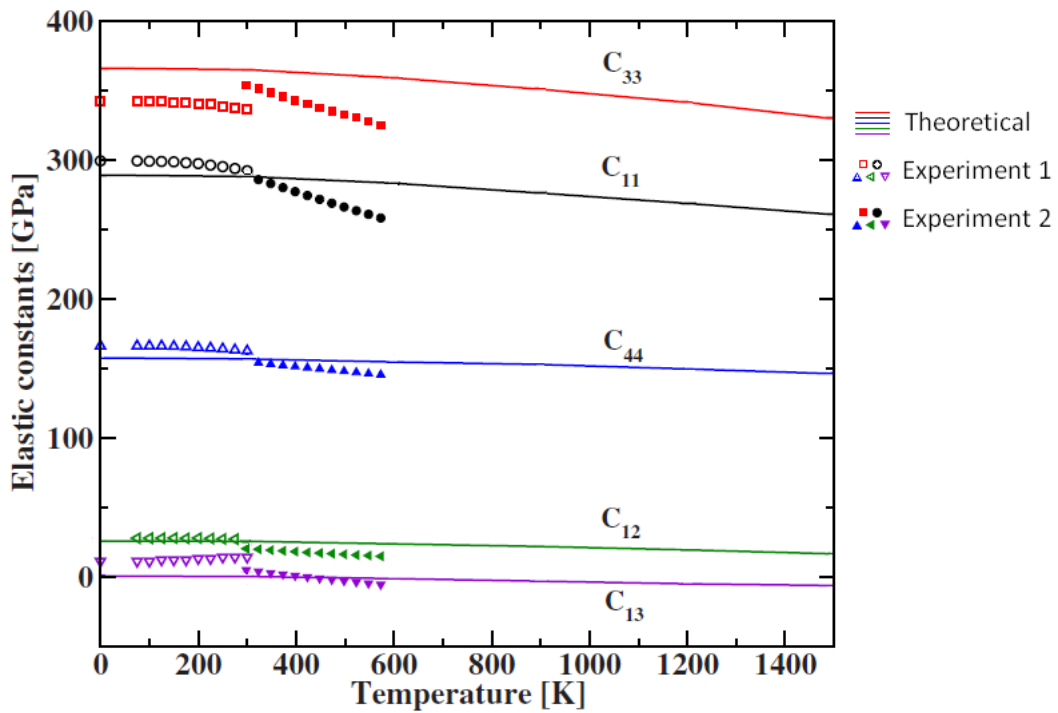


Figure 5: Stiffness constants as a function of temperature. Theoretical results by Kadas *et al.*[29] are represented by lines, experimental data of Smith and Arbogast[23] is denoted by open symbols and measurements of Rowland and White[27] are displayed with filled symbols.

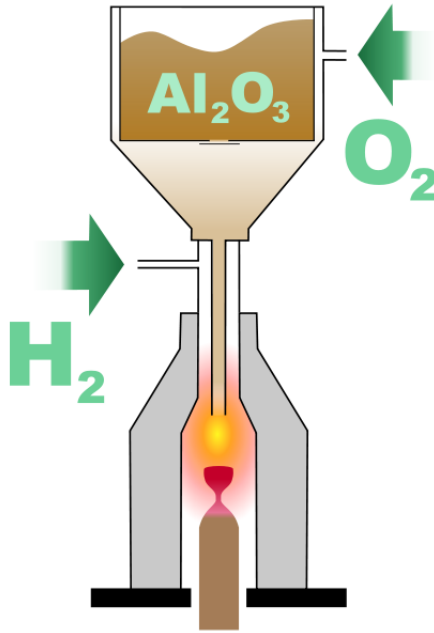


Figure 6: A simplified diagram of the Verneuil process.

a. Flame Fusion Method Also known as the Verneuil Process, the method was developed in 1902 by the French chemist Auguste Verneuil. Figure 6 on page 16 shows a simplified schematic of the Verneuil furnace. Raw materials are fed at the top of the furnace. Hydrogen and oxygen is supplied into the chamber for combustion. At the tip of the narrow tube where combustion takes place, a high temperature above the melting point of the raw materials is maintained. Liquid droplets of the material are collected at the tip of the support structure below. The support is slowly pulled away from the combustion region to allow the liquid to solidify and forms a continuous single-crystal boule. The quality of the crystal depends on the purity of the initial raw material, the pulling velocity and the temperature distribution in the combustion region.

The method is primarily used in the fabrication of synthetic gemstones.[33, 34]

b. Czochralski Method The procedure was developed in 1916 by Polish scientist Jan Czochralski. Figure 7 on page 17 shows a layout of the Czochralski process for production of doped single-crystal silicon.

In the Czochralski method, the raw material is melted into a crucible, and dopants are added if required. A seed crystal, mounted on a rod, is introduced into the melt. The seed crystal's rod is then slowly pulled upwards, allowing solidification of the liquid at the seed-melt interface. The pulling of the rod may be simultaneously accompanied by rotation

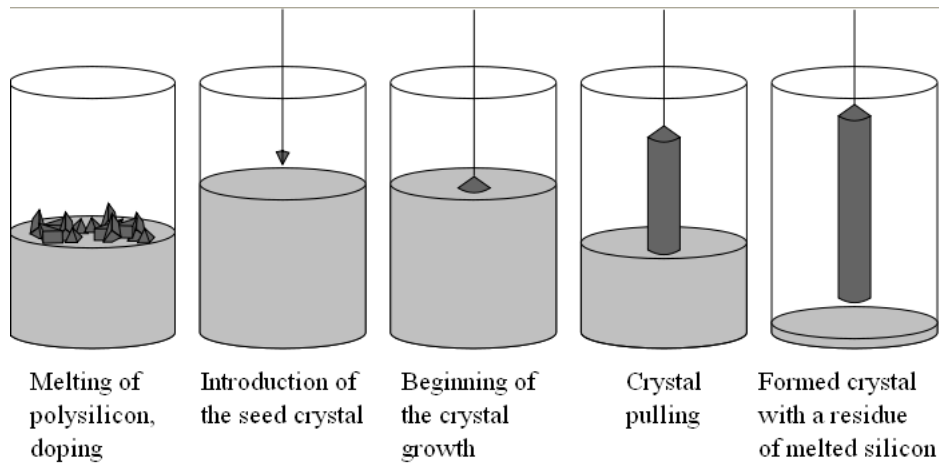


Figure 7: The Czochralski process in the case of silicon.

of the rod, rotation of the crucible or both. As the rod is pulled, the crystal grows, and a cylindrical boule of single-crystal is obtained at the end.

The quality of the crystal depends on the purity of the initial raw materials, the pulling velocity, the rotation speed and the purity of the crucible and of the atmosphere around the crystal. It is also important to orient the seed crystal properly, since the lattice orientation in the final boule directly depends on the original orientation of the seed.

This is the most popular method for the production of large single-crystals, and is most commonly used to manufacture single-crystals of semiconductors and metals.[33, 35]

c. Bridgman-Stockbarger Method In this method, the raw material is sealed inside an ampoule. The ampoule is then placed in a furnace. Figure 8 on page 18 shows a schematic of the furnace. Along the length of the furnace, three separate temperature regions are maintained: the “hot region”, the “temperature gradient region” and the “cold region”. The solid-liquid interface is located in the temperature gradient region.

Initially, the ampoule is inserted in the furnace such that it resides completely in the hot region. The raw material melts giving liquid charge. The ampoule is then slowly moved downward from the high temperature region to the low temperature region, all the while rotating. As the charge passes through the solid-liquid interface, the melt solidifies and starts growing into a single crystal. The interface is moved along the complete length of the ampoule and a single-crystal rod of the material is obtained at the end.

The quality of the crystal depends on the purity of the initial raw material, the pulling velocity, the rotation speed and the temperature distribution in the furnace. The mechanism

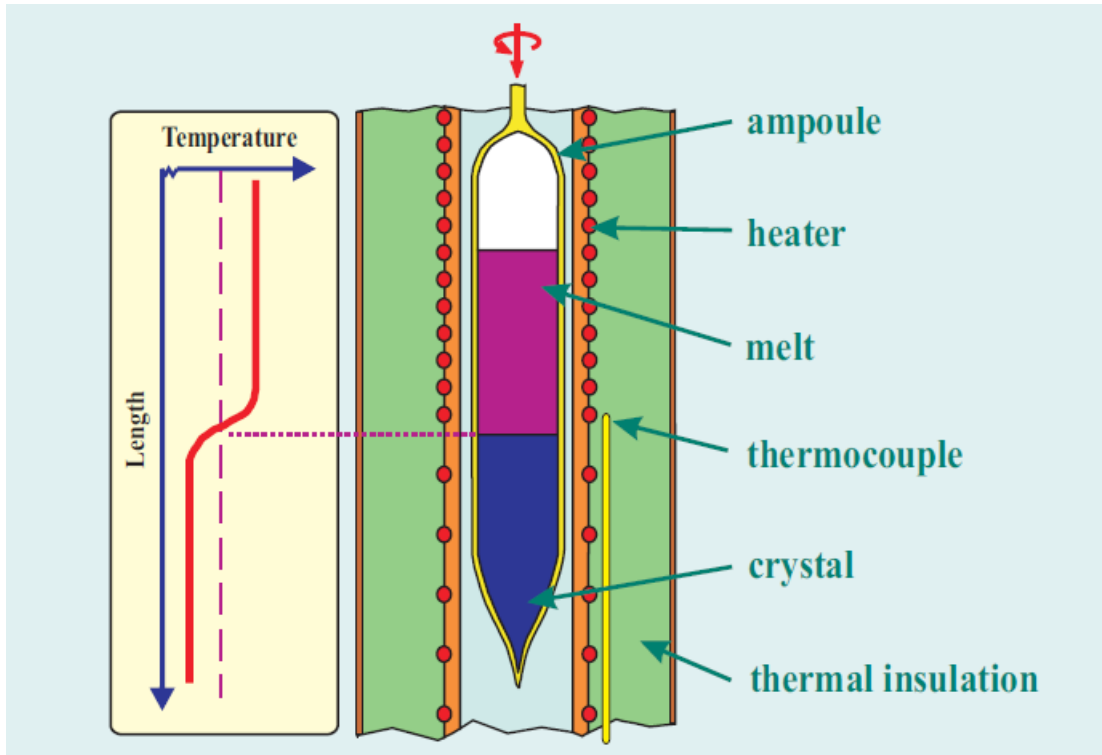


Figure 8: A diagram of the Bridgman-Stockbarger process.

may be used in both horizontal and vertical directions. This Bridgman-Stockbarger method also allows the simultaneous growth of multiple single crystals if several ampoules are placed parallel to each other in the furnace. The method is generally used to manufacture single-crystals not easily obtained from the Czochralski method, for example gallium arsenide.[33, 36, 37]

d. Float Zone Method The float zone method is similar to the Bridgman-Stockbarger method, but instead of melting the entire raw material, the idea is to move a short uniform “molten zone” through the material. The technique was originally employed for purification purposes in a process known as “zone refining”, introduced in the early 1950s at Bell Labs. Figure 9 on page 19 shows the float zone mechanism. The feed rod is placed in a feed rod holder. A small portion of the rod, generally near the bottom, is heated by an RF induction coil to create the molten zone. The feed rod is then slowly moved downward, and may also be rotated at the same time. As the rod is lowered, the molten zone moves along the length of the rod and all the impurities remain within the molten region. Below the molten zone, the material solidifies. Because of the lack of impurities in this region, the boule can grow as a single crystal if a seed crystal is placed at the base. At the end of the process, the

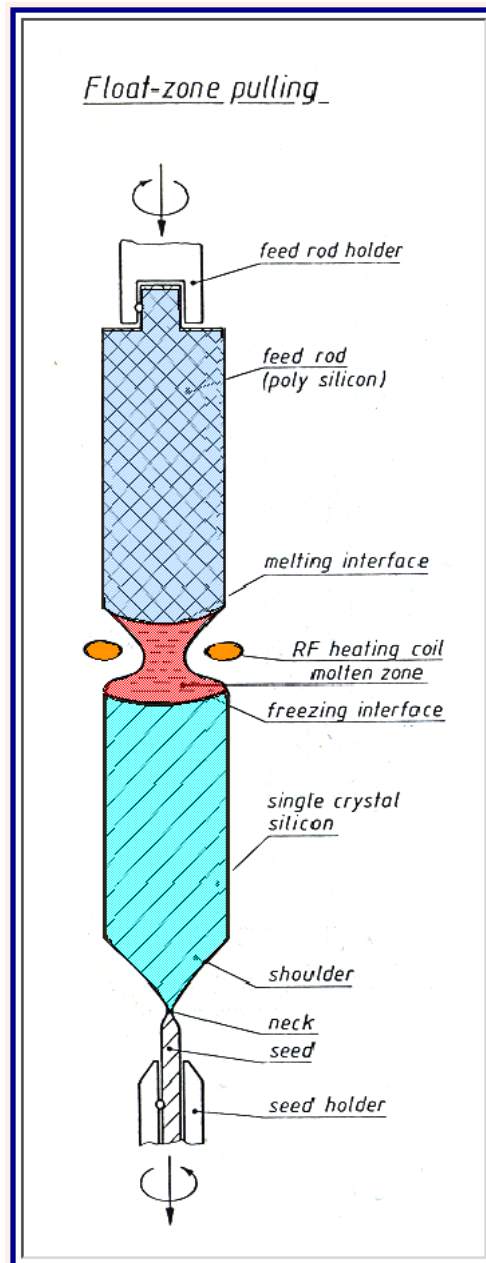


Figure 9: Float zone method.

impurities are segregated to one end of the boule, which may be cut off to give a high purity single-crystal rod. The process may be repeated several times to further remove impurities and defects.

One of the main advantages of this crystal growth scheme is the absence of a crucible or ampoule. This avoids contamination from the crucible, and also ensures that there are no nucleations zones apart from the site of the seed crystal. The monocrystals produced by

the float zone are therefore superior in quality than those manufactured from the methods mentioned earlier.[33, 38–41]

e. Solution Growth Method This method is similar to the Czochralski process. However, instead of melting the raw material in the crucible, the material is dissolved in an appropriate solvent until the solution is saturated. Once saturation is achieved, a seed crystal mounted on a rod is lowered into the solution. For this crystal to grow, the solution needs to be supersaturated. Supersaturation can be achieved by slow cooling of the solution, changing the pH of the solution or introducing another solvent that reduces the solubility of the solute. As the solution is cooled, the solute precipitates and grows on the seed crystal. The seed crystal's rod is slowly pulled out of the solution allowing the crystal to grow uniformly. At the end, one large single-crystal may be obtained.

This method is useful for materials with a high melting point. The limitation however lies in the possible inavailability of appropriate solvents that allow supersaturation and stable crystallization.[33, 42]

C. Fabrication of Single-Crystal Beryllium

1. Production Processes

At present, there are two primary methods of growing large, high purity single-crystals of beryllium for use in scientific experiments:

a. Slow Directional Solidification of Melt in a Crucible This is one of the earliest and simplest methods used to grow beryllium monocrystals. Figure 10 on page 22 shows a sketch of the equipment used for the growth process. A crucible filled with beryllium feed material is placed in a vacuum tight tube. The tube is filled with high purity argon due to the high vapor pressure of beryllium. The feed material is completely melted in the furnace, ensuring that the orientation of grains within the starting material does not influence the subsequent crystal growth. The furnace is slowly raised to allow the directional solidification of the melt. Solidification first begins at the bottom of the crucible. Heterogeneous nucleation occurs at the crucible wall resulting in the growth of several large single-crystal grains in the final ingot. Figure 11 on page 23 shows the granularity of such an ingot. The single-crystals may be extracted from the metal ingot by an appropriate cutting instrument, for

example with a jeweller's saw or a spark-erosion machine for higher precision. The first beryllium monocrystals were grown using this technique[22]. Monocrystals fabricated by this method have been mainly used for investigating the mechanical and fracture behavior of beryllium[21–23, 27, 30, 44, 45] where the perfection of the single-crystals is not vital. The procedure has proved unsuccessful in growing single-crystals of the quality required for neutron monochromators[43].

b. Float Zone Method The floating zone technique has been explained earlier in this paper on page 18. It has by far been the most popular method of manufacturing beryllium monocrystals. After its development in 1952, the zone refining process was employed to grow single-crystal beryllium pieces for use in all sorts of experiments[25, 28, 46–51]. Special precautions are considered while growing beryllium monocrystals by float zone. Due to the high vapor pressure of beryllium, the feed rod is almost always surrounded in a high purity argon atmosphere. The toxicity of beryllium vapor and dust also necessitates that the entire apparatus is housed in an airtight glove box.

A popular variant of the float zone equipment setup uses a double-ellipsoid mirror furnace instead of the traditional RF induction coil to produce the molten zone in the feed rod. Figure 12 on page 24 shows a basic schematic of the double-ellipsoid mirror furnace. The lamps model point sources of radiation surrounded by ellipsoidal mirrors. The radiation reflects off of the mirrors and is concentrated on a particular region of the feed rod, heating it up to create the molten zone. The equipment is described in detail by Eyer *et al.*[53]. The double-ellipsoid mirror furnace avoids vibrations produced by the alternating electromagnetic field in an induction heated facility. Because the furnace also affords excellent control of crystal diameter, the necking process can be implemented to reduce the defect concentration in the crystal[43, 54]. With these added benefits, float zone with double-ellipsoid mirror furnace has been successfully employed to grow beryllium single-crystals with defect concentrations suitable for use in neutron monochromator applications[43, 54, 55]. These crystals can also be used as high flux X-ray monochromators, but further improvement in crystal quality and increased understanding of the defect structure is needed for use in synchrotron radiation optics[54].

An experimental investigation has shown that there is no preferred direction for the growth of beryllium single-crystals[43]. With the use of a properly oriented seed crystal, it is possible to grow beryllium single-crystals of any desired orientation[43, 56]. In the

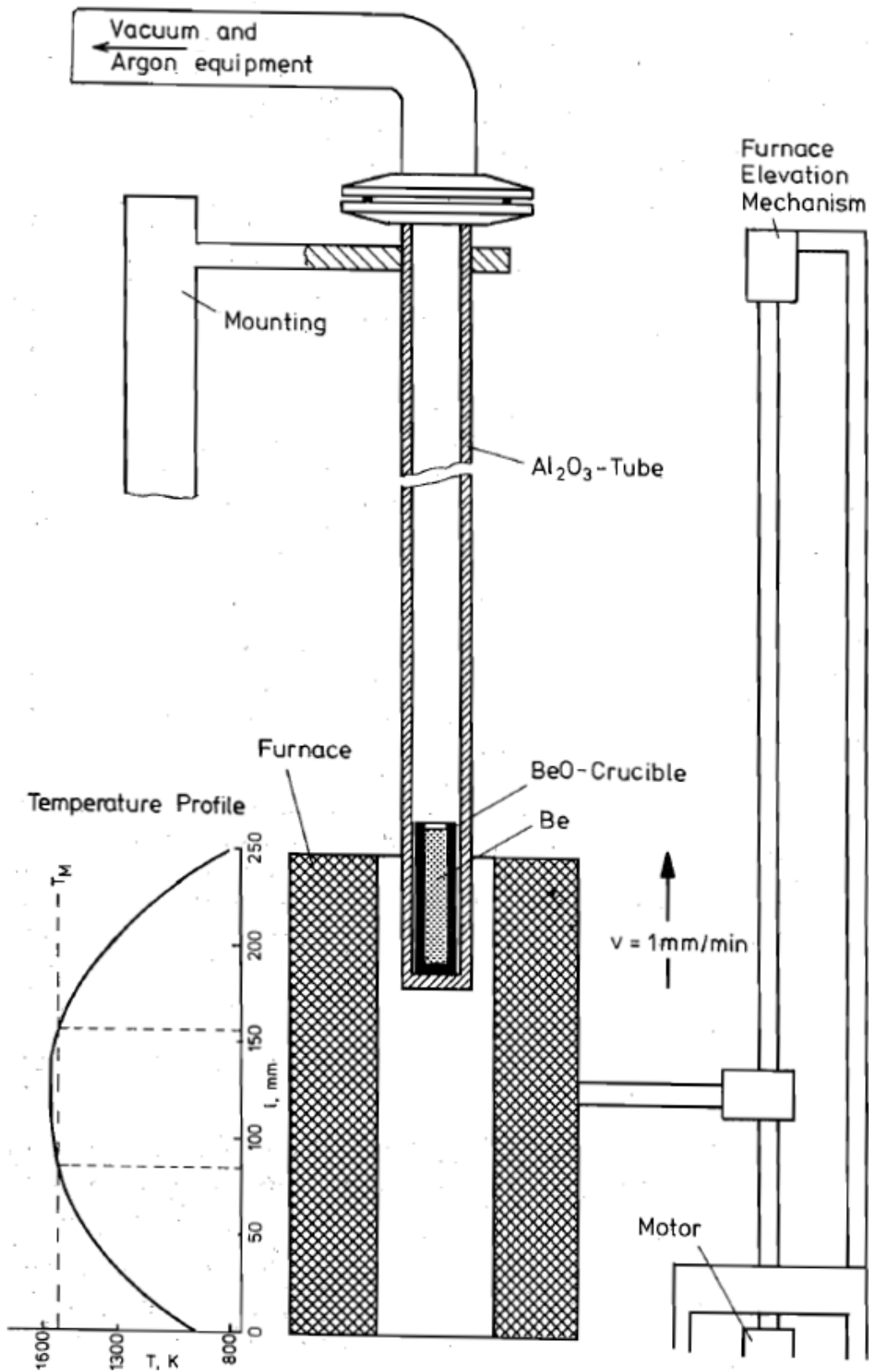


Figure 10: Sketch of directional solidification equipment and temperature profile of the furnace.[43]

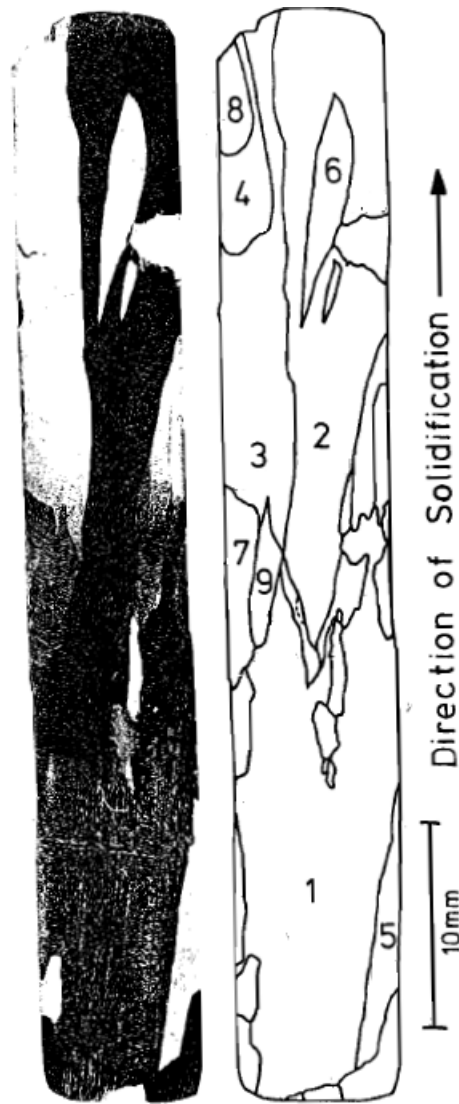


Figure 11: Microstructure of a directionally solidified beryllium rod. Numbers 1-9 indicate the large single-crystal grains.[43]

absence of a seed crystal however, the orientation of the monocrystal will be determined by the orientation of the pre-existing grains in the feed rod. It is worth noting that in the past, extruded beryllium stock has often been used as feed in the float zone procedure. The extrusion process results in the grains being oriented in a particular direction within the rod. Therefore when these rods are used in float zone, the resulting single-crystals have a growth direction almost always parallel to the basal plane[43].

Experiments have also established guidelines about the growth velocity and rotation velocity of the seed crystal mount, as well as the usefulness of the necking technique. A growth velocity of 1mm/min is considered ideal[54]. A higher velocity disrupts the single-

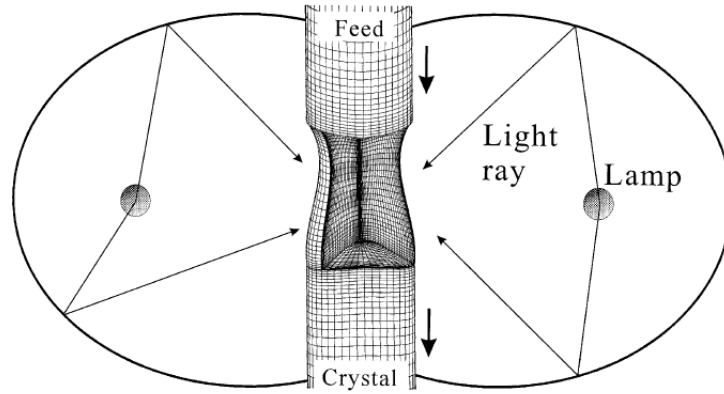


Figure 12: Schematic of floating-zone crystal growth in a double-ellipsoid mirror furnace.[52]

crystal growth, but a lower velocity is not seen to improve the crystal quality. In order to get a uniform temperature distribution across the molten zone, it is also necessary to rotate the seed crystal, but no particular dependence on rotational velocity is observed[54]. Lastly, the necking technique is only deemed useful if the seed crystal contains several grains. The necking ensures that only one of the grains will propagate and grow into the single-crystal boule[54]. If the seed crystal is already single-grained, then necking is not required.

Once the single-crystals have been grown by either melt solidification or float zone, they are cut and shaped into a specific geometry required for the experiment. Often the crystals are worked into a rectangular cross-section with the c -axis parallel to one edge of the rectangle, with opposite faces ground closely parallel[23, 27]. After obtaining the required geometry, the metal is chemically etched and polished for greater crystal perfection. A metal specimen may be coated with another material for protection against scratching or surface damage.

2. Production History

Since the early 1950s, samples of beryllium single-crystals have been manufactured for use in scientific experiments. The earliest beryllium monocrystals were obtained by cutting from large-grained cast ingots grown by melt solidification. With improving technology and increasing demand for better crystals, the float zone process became more widespread and established itself as the leading beryllium crystal growth mechanism in the 1970s. Instead of growing their own beryllium monocrystals however, the scientific community opted to pur-

chase or loan the material from established manufacturers instead. The Franklin Institute[57] was the largest producer of zone refined beryllium single-crystals in the latter half of the twentieth century. Other manufacturers mentioned in the references include Nuclear Metals, Inc.[58], The Benjamin Franklin Institute of Technology[59] and Brush Wellman Inc. Electrofusion Products[60]. Information about other national or international manufacturers of single-crystal beryllium is not currently available.

In the past couple of decades, the semiconductor microprocessor industry has grown tremendously thanks to the large-scale production and availability of single-crystal silicon wafers. Unfortunately, this has not been the case with beryllium. High quality beryllium monocrystals are still generally expensive and difficult to acquire. A single-crystal beryllium rod of approximately 15mm diameter and 25mm length will cost approximately \$30,000 a piece[61]. In comparison, a single-crystal silicon piece of the similar dimensions and quality costs less than \$10 a piece[62–64].

The epitaxial growth of single-crystal beryllium films was first reported in 1992 by a group of scientists from the University of Arizona, Tucson[65]. Single-crystal films were grown on α -Al₂O₃(sapphire), silicon and germanium substrates at several different substrate temperatures and deposition rates, and the various results were published in a series of papers[65–70] between 1992 and 1994. It was determined that beryllium forms an epitaxial overlayer with Be(0001) layer parallel to α -Al₂O₃(0001), Si(111) and Ge(111). *In situ* and *ex situ* analysis on the films indicated that all beryllium layers grown were high quality single-crystals. The crystal perfection was better for Ge than for Si, which in turn was better than for α -Al₂O₃[70]. This is attributed to the small lattice mismatches between beryllium and the substrates. The lattice mismatches for Be (0001) with α -Al₂O₃(0001), Si(111) and Ge(111) are 3.9%, 3.4% and 1.0% respectively[70]. A direct relation was also observed between crystal quality and the substrate temperature at the time of crystal growth. The films were grown with temperatures between 100^oC and 500^oC. The structural coherence length and therefore the crystal quality was observed to increase with increasing temperature. At the same time however, formation of discontinuous “islands” instead of a continuous Be film was seen for temperatures beyond 300^oC. In the case of Si(111) and Ge(111), the film surface also became visibly rough at these high temperatures. Such unwanted features degrade the overall quality of single-crystal films. Table VI on page 26 shows the best growth temperature for each substrate material as determined by x-ray diffraction and ion beam

Substrate	Growth Temperature ($^{\circ}\text{C}$)	X-ray Diffraction Rocking Curve FWHM	Ion Beam Channeling χ_{\min}
$\alpha\text{-Al}_2\text{O}_3$	125	0.51 ± 0.02	0.81 ± 0.02
Si	300	0.24 ± 0.02	0.33 ± 0.02
Ge	300	0.19 ± 0.02	0.18 ± 0.02

Table VI: Summary of best Be films grown on each of the three substrates.[70]

channeling parameters. The best films were grown on Ge(111) at 300°C .

V. CONCLUSION

With improved zone refining technology and the mirror furnace float zone technique, it is possible to grow beryllium crystals without sub-grains and with a low defect density. With these high quality crystals now available, it is worthwhile to investigate the application of monocrystal instead of polycrystal beryllium in x-ray windows. The lack of grain boundaries within the single-crystal lattice would afford improved x-ray transmission and avoid unwanted attenuation due to scattering of the x-rays. Also, development of beryllium for monochromator applications in synchrotron facilities looks promising. Experiments need to be conducted on available crystals to ascertain their performance in lens and monochromator applications. Further theoretical and experimental investigations are also required to understand and influence of impurities and defects on the x-ray characteristics of beryllium.

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