

[54] **METHOD AND APPARATUS FOR GROWING CRYSTALS BY ANNEALING THE CRYSTAL AFTER FORMATION**

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[57]

ABSTRACT

This invention is directed toward a method and apparatus for producing fracture-free crystalline boules through a simultaneous growing and annealing technique. It involves a conventional flame-fusion crystal-growing process and apparatus modified to effect crystal growth by using a high temperature fusion flame within a controlled heated zone. The temperature of the zone is controlled in the top portion at a temperature sufficient to effect crystal growth and in the bottom portion at a temperature sufficient to effect a complete anneal of the grown crystal. The device of this invention comprises a conventional Verneuil type crystal growing apparatus modified by the addition of a high temperature furnace arranged concentrically around the growing chamber. The growing chamber comprises an elongated tube of high temperature resistant material, such as zirconia, positioned and aligned directly below a powder dispensing assembly and burner assembly. The growing chamber passes through the center of the furnace which includes a high temperature tungsten mesh heating element, heat shields and a water-jacketed cover.

2 Claims, 2 Drawing Figures

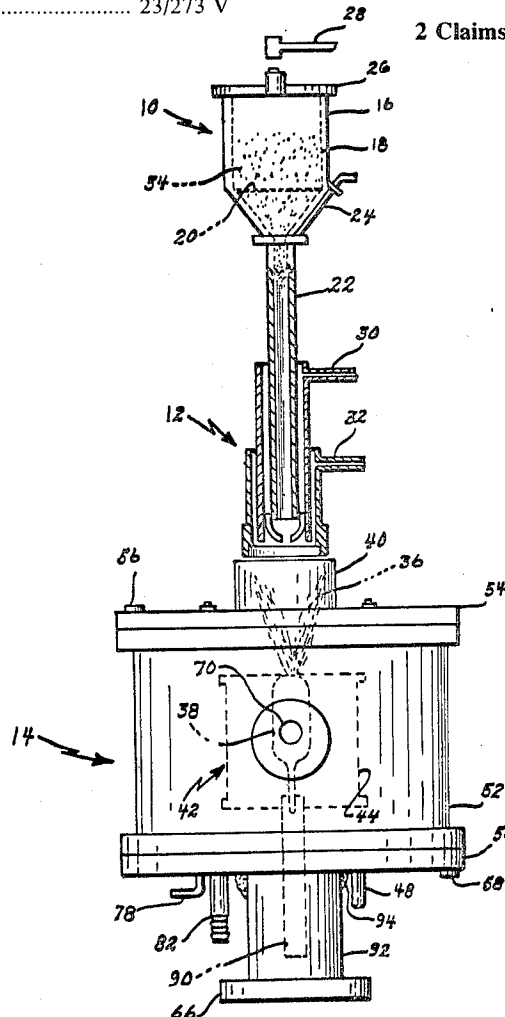


FIG. 1

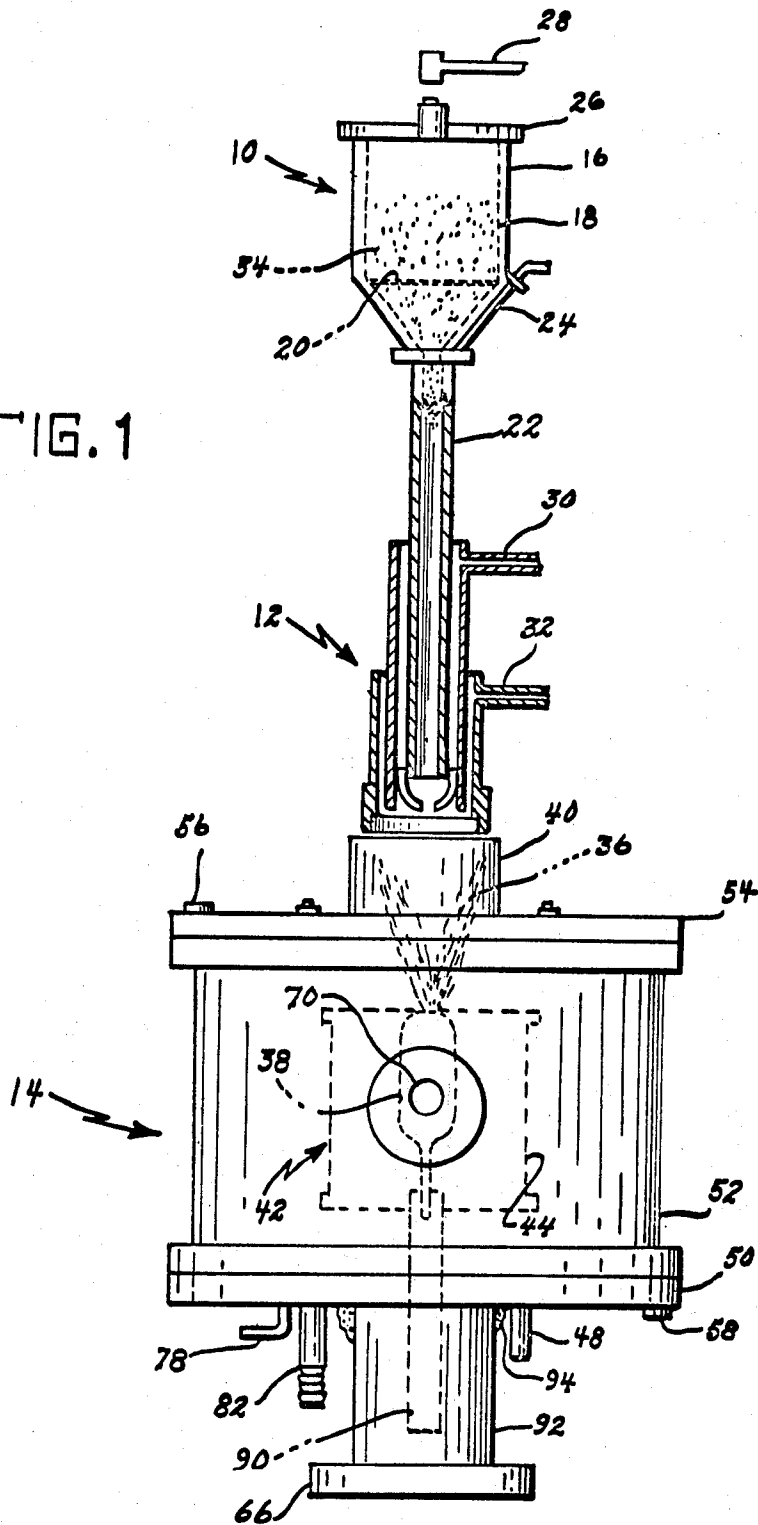
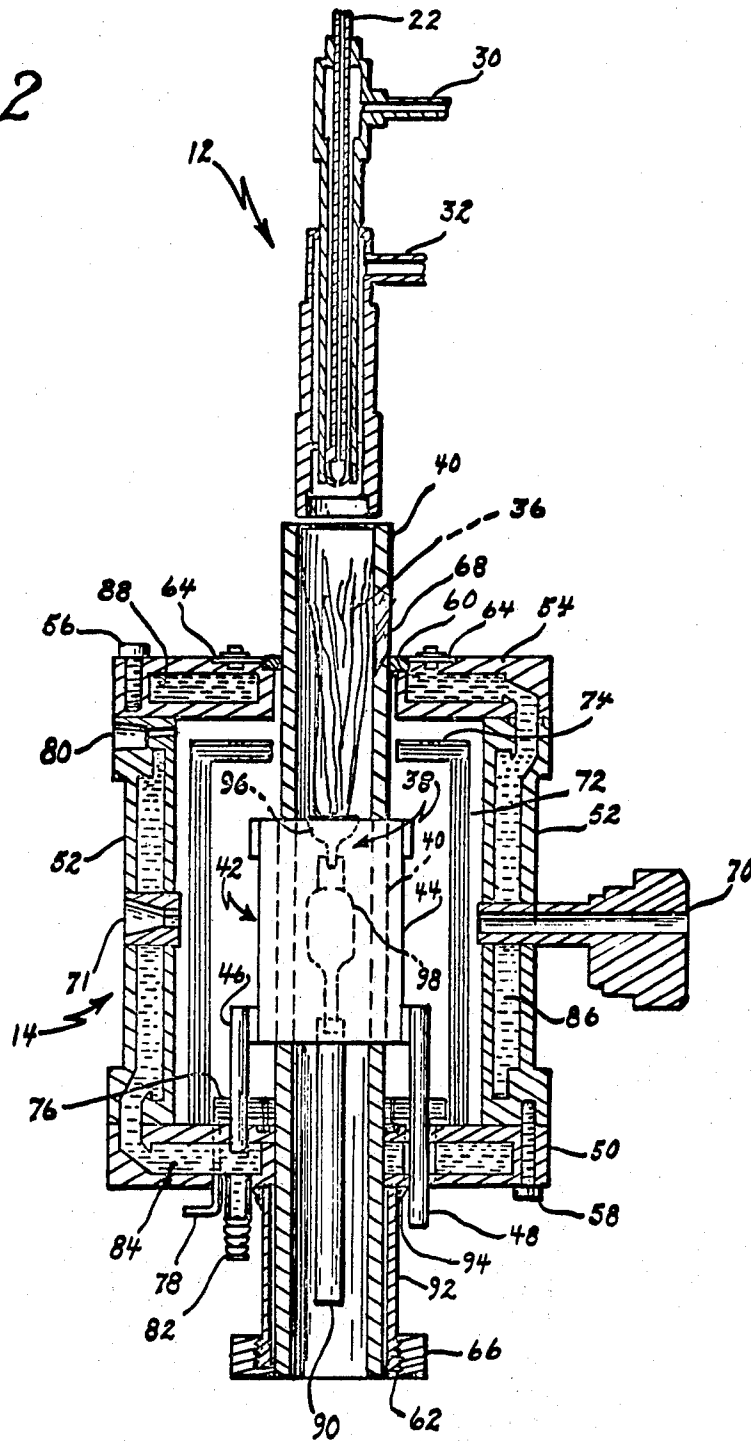


FIG 2



METHOD AND APPARATUS FOR GROWING CRYSTALS BY ANNEALING THE CRYSTAL AFTER FORMATION

BACKGROUND OF THE INVENTION

This invention relates to an apparatus and method for growing synthetic crystalline boules. More particularly, this invention concerns itself with an apparatus and method for growing fracture-free, single crystals by the well-known Verneuil flame-fusion crystal growing process.

Synthetic sapphire, ruby and other crystalline materials, such as spinel and rutile, have been grown heretofore by a high temperature fusion process. This process, often referred to as the Verneuil process, is well known and comprises the steps of passing powdered oxide through a high temperature zone and then introducing them into a crystal growing zone where crystal growth is achieved by a controlled melting and recrystallization of the powdered oxides. In this type of process, the high temperature necessary to melt and fuse the powdered oxides may be provided by means of a radio frequency heater, a furnace, an arc or a flame. One of the most effective methods involves the use of an oxy-hydrogen flame.

In the flame-fusion method, the powdered feed constituents are placed in a vertical container aligned axially above the flame which, in turn, is aligned axially above a crystal growing surface. The powder is allowed to fall through the flame which impinges upon the growing surface. The powder is melted and fused in the intense flame and collects on the crystal-growing surface of a support rod where it adheres and slowly forms a carrot-shaped mass, called a boule. The support rod is then gradually lowered away from the flame by a suitable retraction mechanism so that only the growing surface of the boule is maintained in a molten state. When a crystal of sufficient size is grown, the furnace is shut down and allowed to cool for a short time. The boule is removed and further cooling takes place rather rapidly.

Flame fusion grown crystals, however, often crack when cooled. The resulting fragments, while satisfactory for some purposes, are unsatisfactory for laser and maser applications which require the use of relatively large crystals substantially free from defects. Consequently, single crystals grown at high temperatures must usually be annealed if they are to be used for technical applications. The temperature at which the crystal is usually annealed approaches the melting temperature of the crystal and the annealing process relieves strains developed during growth. This prevents or at least minimizes, the chance of fracturing the crystal during mechanical working. Also, the annealing step reduces the number of dislocations in the grown crystal.

Heretofore, the annealing step took place in a separate furnace after the crystal had been grown and cooled. As a result, considerable time and expense was involved in bringing the cooled crystal up to an annealing temperature and then subjecting it to a slow and controlled cooling to effect a proper anneal. In order to minimize the time required for growing and annealing, it has been suggested that castable alumina muffles, alumina fire brick, or after heaters be affixed to a conventional Verneuil apparatus at a point immediately below the crystal growing chamber. The sugges-

tions were made in order to contain the heat and effect an anneal of the crystal after growth formation. However, only partial annealing of the crystal could be accomplished by such devices and a further and final annealing step had to be carried out in a separate furnace. The separate annealing step not only involves additional time and expense but also increases the chance of crystal fracture because of the necessity for cooling and then reheating to the annealing temperature.

With the present invention, however, the disadvantages encountered when employing a separate annealing technique have been overcome by providing a Verneuil apparatus and process with a modification that permits the steps of crystal growing and annealing to be accomplished simultaneously.

A separate high temperature electric furnace is positioned concentrically around an elongated growing chamber. The temperature within the growing chamber is set at a predetermined figure, usually the annealing temperature of the material being grown and maintained at that temperature throughout the chamber. This produces uniform temperature gradients throughout the length of the chamber and establishes a longitudinal uniform heat zone. The growing crystal descends through the controlled heat zone resulting in a simultaneous growing and annealing process.

This invention provides the means for growing and annealing a crystal in one step. There is no need for a separate annealing step and the high fracture rate often encountered with prior art devices is almost eliminated. The apparatus of the invention is capable of simultaneously attaining a temperature of 2,040°C and a temperature of 1,950°C within an elongated growing chamber thereby eliminating the separate annealing furnace heretofore required for growing high quality corundum crystals.

Thermal gradients within the growing chamber are significantly reduced and the rapid quenching of the grown crystal, which normally follows the shut-down of a conventional Verneuil apparatus, is eliminated. This minimizes the major causes of internal stresses and strains that occur in crystals during flame fusion growth.

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been found that fracture-free, single crystal boules of high quality and unusual length can be grown in a Verneuil-type, flamefusion apparatus modified in such a manner that the crystal is grown and annealed simultaneously. Normally, the crystal is formed and grows at the top of a support rod, or crystal growing surface which, in turn, is positioned axially underneath an intense oxy-hydrogen flame. As the crystalline material forms, it is slowly withdrawn downwardly away from the flame so that only the top growing surface of the crystal remains within the flame. The remaining portion of the crystal is withdrawn into an area protected by a heat shield, such as an alumina muffle, in order to provide an atmosphere that permits the crystal to be cooled slowly over a relatively long period of time.

With the present invention, however, the crystal growing chamber, in addition to utilizing an oxy-hydrogen flame for effecting crystalline growth, also includes an elongated, high temperature electric furnace which is positioned concentrically around an elongated crystal growing chamber. The furnace gener-

ates and maintains a controlled temperature environment uniformly throughout the length of the chamber. Crystal growth occurs in the chamber at a position located adjacent to the top of the elongated heater under controlled temperature conditions. As growth continues, the growing crystal is progressively retracted at a controlled rate into the growing chamber, the temperature of which is controlled and maintained at that temperature required for completely annealing the crystalline material being grown. As a consequence, thermal gradients within the growing and annealing zone of the growing chamber are carefully controlled with no temperature interferences occurring in either the crystal growing or crystal annealing environment.

Accordingly, the primary object of the invention is to provide an improved apparatus and method for growing crystalline material of gem-like quality.

Another object of this invention is to provide an improved apparatus and method for growing fracture-free, synthetic crystalline materials of relatively large size.

Still another object of this invention is to provide an improved apparatus and method for effecting the simultaneous growth and anneal of single crystals.

The above and still further objects and advantages of the present invention will become readily apparent after consideration of the following detailed description thereof when taken in conjunction with the accompanying drawings.

DESCRIPTION OF THE DRAWINGS

In the drawings:

FIG. 1 is a plan view, partially in cross-section, of a flame-fusion crystal-growing apparatus modified in accordance with this invention; and

FIG. 2 is an enlarged plan view, partly in cross-section, showing a flame-fusion crystal-growing chamber modified by the addition of a high temperature furnace.

In FIGS. 1 and 2, like elements are represented by like numerals.

Referring to the drawings, FIG. 1 shows in general the details of a Verneuil-type, flame-fusion apparatus modified by the addition of a high temperature furnace, positioned concentrically around the crystal-growing chamber of the apparatus. The apparatus described comprises a powder dispensing assembly 10, a gas burner assembly 12, a crystal-growing and annealing assembly 14, and a conventional retraction assembly, not shown. The dispensing assembly 10 comprises an outer housing 16 and a funnel-shaped inner powder feed container 18 for holding the powdered oxides 34 which will ultimately form the desired crystal boule. A fine mesh wire screen 20 is located in the bottom portion of the container 18. An elongated tube 22 extends downwardly from the powder dispensing assembly 10 to the growing and annealing assembly 14. The outer housing 16 is provided with an inlet 24 for the introduction of a carrier gas to the assembly 10. In this invention, oxygen is used as the carrier gas although other gases could also be employed. A cover 26 for effecting a gas-tight seal is affixed to the top of housing 16. A conventional knocker or tapper 28 is suitably connected by electrical or mechanical means, not shown, for causing the tapper 28 to fall periodically and strike the cover 26. The periodic tapping in a controlled manner causes the powdered feed constituents to flow downwardly through the burner assembly 12 from the

powder container 18 to the growing and annealing assembly 14.

The gas burner assembly 12 is positioned in axial alignment below and connected to the dispensing assembly 10. It extends toward and terminates at the top portions of the assembly 14. It comprises a conventional three-tube oxy-hydrogen gas burner and, in essence, is an inverted blow-pipe which produces an intensely hot flame 36 by using a mixture of hydrogen and oxygen gases. Gas burners, other than the three-tube device, utilized herein could likewise be employed to produce the high temperatures needed to form a crystal boule.

The burner 12 is provided with an inlet 30 for the introduction of hydrogen gas and an inlet 32 for the introduction of oxygen gas, hereinafter referred to as the outer oxygen gas. The oxygen carrier gas, which enters the apparatus at inlet 24 and will hereinafter be referred to as the inner oxygen gas, not only entraps and aids in directing the flow of the falling powder 34 toward the growing assembly 14, but also contributes to the production of the intensely hot flame 36.

The growing and annealing assembly 14 comprises, in general, a crystal-growing zone 38 positioned within a cylindrical tube 40 composed of zirconia. The tube 40 passes through the center of a high temperature electric furnace 42. By referring to FIG. 2, it can be seen that the furnace 42 consists of a cylindrical tungsten mesh heating element 44, affixed to support legs 46 and 48 which, in turn, are inserted into holes drilled in the bottom plate 50 of a water-cooled jacket 52. Leg 48 also acts as an electrode and is connected to a suitable source of electrical power, not shown, which maintains and controls the degree of heat within the growing and annealing assembly 14. The support legs 46 and 48 are electrically insulated from the water-cooled jacket 52.

Various valve means and manometers, not shown, control the flow of calibrated amounts of hydrogen, inner oxygen and outer oxygen gases through the inlets 30, 24 and 32, respectively.

The water-cooled jacket 52 includes a water-jacket top cover 54 affixed thereto by bolt 56 and a water-jacket bottom cover 50 affixed thereto by bolt 58. The growing and annealing assembly 14 is ring-sealed top and bottom at 60 and 62 where it passes through the water-jacketed top cover 54 and bottom cover 50 to form a gas-tight seal. Retaining ring 64 and backing nut 66 hold the O-rings 60 and 62 in sealed relationship.

The zirconia tube 40 extends above the top of and below the bottom of assembly 14. A small viewing hole 68 is drilled at an angle through the tube 40 to permit visual inspection of the crystal during the growing of the boule. A viewpoint 70 is provided to enable the measurement of the temperature on the zirconia tube 40 by means of an optical pyrometer. A thermocouple port 71 is drilled through water-jacket 52 to permit automatic temperature control within the growing and annealing zones. The temperature within the growing and annealing zone is automatically monitored and controlled by a conventional controller and programmer through the thermocouple port 71 and a silicon controlled rectifier connected to an outside source of electrical power, not shown.

An argon atmosphere is maintained within the assembly 14 during the growth operation to prevent oxidation of heating element 44 and heat shields 72, 74 and

76. A gas inlet 78 located at the bottom cover 50 and a bleed outlet 80 located at the top of jacket 52 of an inert gas, such as argon, can keep air from leaking in. This allows for atmosphere control and allows the furnace to be kept at a positive pressure during operation.

The assembly 14 is connected to a chilled water circulating system at inlet 82 that isolates the heat and confines it within assembly by means of water-containing chambers 84, 86 and 88.

Surrounding the heater element 44 and crystal-growing chamber 40 is a heat shield 72 which comprises five cylindrical molybdenum sheets arranged concentrically around the furnace element 44. A top heat shield 74 and bottom heat shield 76, each comprised of five sheets of molybdenum, are positioned at the top and bottom of the furnace as part of the heat shield. Each sheet of shields 72, 74 and 76 are spaced from each other by spacing means, not shown. The heat shields aid in confining the heat within the growing and annealing zone of tube 40. A ceramic support rod 90 provides a crystal-growing surface for the growing boule and is positioned within the center of the tube 40. The rod 90 is, in turn, suitably connected to a conventional retraction mechanism, not shown.

In the apparatus of this invention, crystal growth occurs within the tube 40 at a position 38 located at and adjacent to the top of the furnace element 44. A metal tube 92 surrounds the bottom portion of the tube 40 and is likewise water-cooled by water-containing metal coils, not shown. The tube 92 is soldered at 94 to the water-jacket bottom plate 50 to provide a gas-tight seal.

In the operation of the apparatus of this invention, a C-axis (0°) oriented sapphire seed rod was mounted on the top surface of ceramic tube 90 and raised into the growing position indicated at 38. The assembly 14, prior to growth, is evacuated and back-filled with an inert gas, such as argon, several times after which a positive pressure is maintained to prevent oxidation of the molybdenum and tungsten furnace parts. The temperature of the growing and annealing zone located within the furnace 44 is raised 200°C per hour to the degree of heat needed to accomplish a proper anneal which in the case of sapphire is $1,950^\circ\text{C}$.

The three-tube post mix oxy-hydrogen burner 12 is then ignited and the rate of flow of gases through inlets 24, 30 and 32 are adjusted to the typical flow rates used for achieving a temperature of $2,040^\circ\text{C}$ needed to grow a sapphire crystal. At this point, the top of the sapphire seed rod forms into a molten ball. Powder drop is then started and the powder 34, in this case purified corundum, flows downwardly through flame 36 and impinges on the sapphire seed. As the crystal grows into a boule, as indicated at 96, the retraction mechanism starts and withdraws the growing boule downwardly so that only the top portion of the boule 96 remains in a molten condition with the bottom portion now in the annealing environment. After a sufficient period of growth, the powder drop is stopped. The grown boule is then lowered at about 5 cm per hour from the growing position indicated at 38 to a position completely within the chamber and controlled temperature zone indicated at 98. The burner gases are gradually decreased and finally shut off to prevent thermal shock to the tube 40 where it protrudes through the top of the assembly 14. The crystal is maintained at the annealing temperature of $1,950^\circ\text{C}$ for about $\frac{1}{2}$ hour. The temperature is then

slowly reduced at a programmed rate of about 200°C per hour to room temperature.

Upon removal from the growing and annealing zone of the apparatus, the sapphire crystal was found to be well shaped and highly polished. A Laue X-ray diffraction pattern indicated that the 0° orientation of the seed was maintained. The crystal was placed in a cell containing diiodomethane, which has the same index of refraction as sapphire, and examined under 10X magnification. The examination revealed no bubbles or powder inclusions.

Without any additional annealing, several slices were cut from the boule along planes perpendicular to the C-axis. The surfaces of these basal planes were then mechanically polished. Unannealed crystals always cleave when subjected to similar conditions. However, the crystals grown in accordance with this invention did not cleave or fracture.

To further illustrate the mode of operation of the apparatus and method of this invention, reference is made to the following in which a sapphire boule having a diameter of $\frac{5}{8}$ inches and a length of 1 inch was grown from a sapphire seed and pure alumina powder in about 3 hours. Typical conditions during growth were gas flow rates of 3 liters per minute for the inner oxygen, 4 liters per minute for the outer oxygen, and 18 liters per minute for the hydrogen, together with a tap rate of about 14 taps per minute. A 60 mesh wire screen was used. The gas flows were regulated at one atmosphere pressure to produce a growth temperature of $2,040^\circ\text{C}$. This temperature was maintained in the growing zone for the 3 hours' growing period. As the crystal grew, it was lowered at a retraction rate of $\frac{3}{10}$ of an inch per hour until the growth period was completed. The crystal was then withdrawn completely into the controlled heat zone and maintained at the soak temperature of $1,950^\circ\text{C}$ for $\frac{1}{2}$ hour after which the crystal was cooled by slowly reducing the temperature at a programmed rate of 200°C per hour to a temperature of 100°C . The furnace was shut down and the boule allowed to cool to room temperature. Crystal growth occurs within both the flame and the temperature control zone, rather than in just the flame as in a conventional flame-fusion apparatus. The resultant sapphire boule was examined and found to be fracture-free with no bubbles or powder inclusions.

The conventional Verneuil method and apparatus usually requires simultaneous shut-down of burner gases. This results in rapid quenching of the crystals and formation of hoop stresses which cause internal strains and fracturing. The improved flame-fusion growing and annealing apparatus of this invention, however, minimizes the steep thermal gradients encountered in prior art devices. This prevents the normal fracturing of the crystal which has often occurred in the past when 0° (and other orientation) crystals have been grown using a typical Verneuil apparatus. Another advantage of the high temperature furnace modification of this invention is that it makes possible the growth by flame-fusion of other single crystals and orientations that have previously been unsuccessful because of attendant high fracture rates. The growth of such crystals only requires minor changes in the temperatures utilized for growing and annealing.

With this apparatus, temperatures of $2,200^\circ\text{C}$ and longitudinal uniform heat zones up to 8 inches long are readily attainable. Effective control of the various

growth and annealing parameters is achieved without any interference with the crystal-growing and annealing environment. This results in the growth of relatively large, fracture-free crystals of gemlike quality that are particularly useful for various technical applications such as for lasers, masers, modulators, deflectors, acoustic materials and electronically active materials.

We claim:

1. A method for simultaneously growing and annealing a fracture-free monocrystalline body in a crystal-growing zone which includes a high temperature flame, and an elongated chamber having a crystal-growing surface positioned within said chamber in axial alignment with said flame, which comprises the steps of: passing a flow of powdered oxide material through the high temperature flame to fuse said material, directing said flame and fused material toward the crystal-growing surface, depositing and accumulating said fused material onto said growing surface at a temperature and for a time sufficient to grow a monocrystalline body thereon while simultaneously lowering said growing body at a rate sufficient to maintain a predetermined distance between the flame and the top portion of the growing body, continuing to lower the growing body while simultaneously providing additional heat to the crystal-growing zone to achieve a predetermined temperature therein, maintaining and controlling said predetermined temperature for a time sufficient to attain the simultaneous growth and anneal of a mono-

crystalline body of desired length, stopping said powder flow, continuing to lower said grown monocrystalline body onto said crystal-growing zone while simultaneously maintaining said predetermined temperature annealing environment, simultaneously stopping said crystal movement and said flame while continuing to maintain said grown crystal in said predetermined temperature annealing environment, cooling said crystal to complete said anneal by reducing said predetermined temperature to room temperature slowly at a programmed rate, and removing the grown and annealed crystal from said growing zone.

2. In a flame-fusion crystalline growing apparatus having a powder dispensing assembly, a gas burner assembly, and a crystal-growing assembly, the improvement which comprises the addition of an annealing assembly surrounding said crystal-growing assembly, said annealing assembly comprising a high temperature electric furnace having a cylindrical tungsten mesh heating element positioned concentrically around said growing chamber, a heat shield surrounding said heating element and spaced therefrom said heat shield comprising a plurality of concentrically arranged cylinders spaced from each other, top and bottom portions each comprising a plurality of cylindrical sheets in spaced relationship to each other, and a water-cooled jacket surrounding said heat shield in spaced relationship thereto.

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