

Feb. 8, 1966

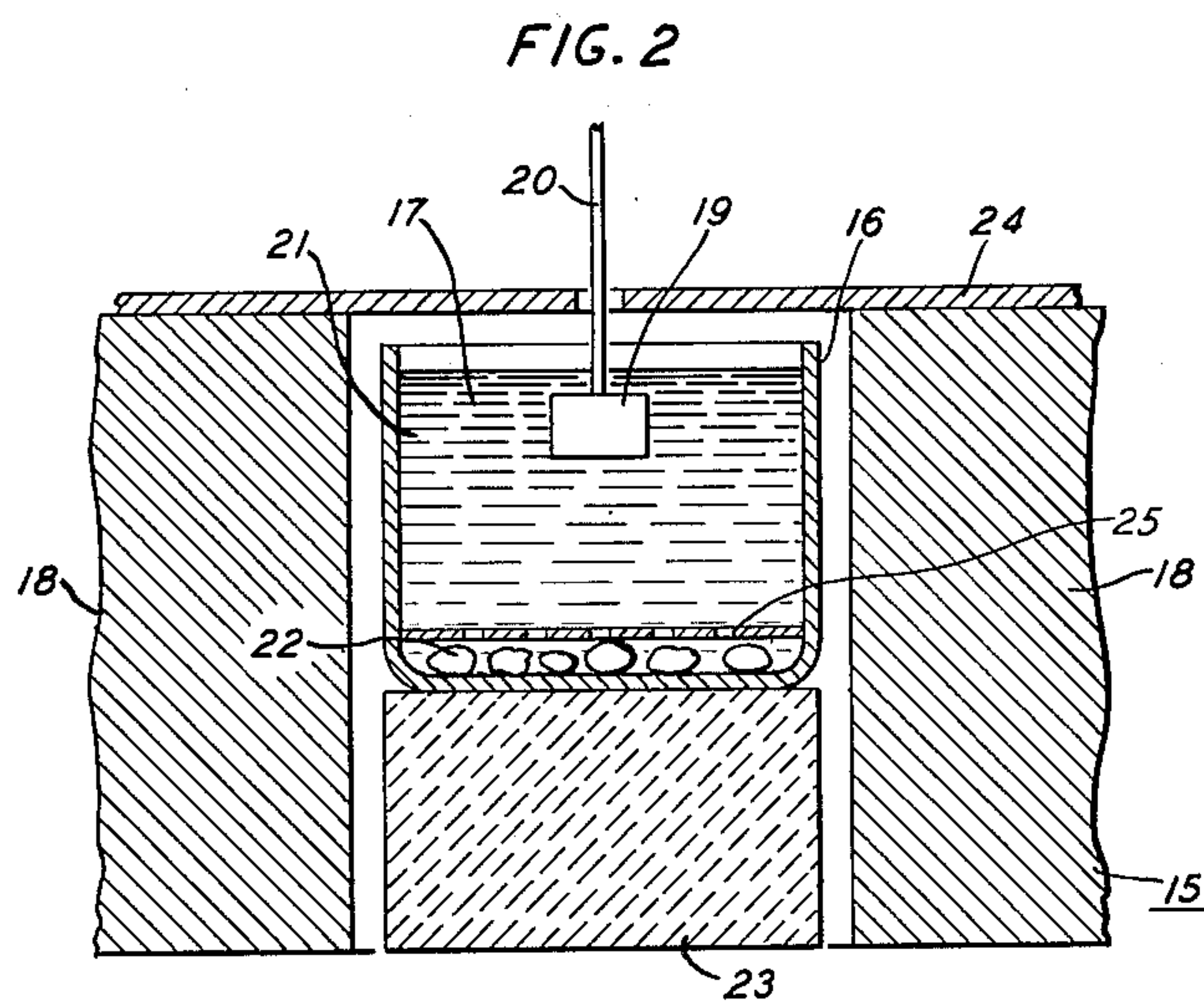
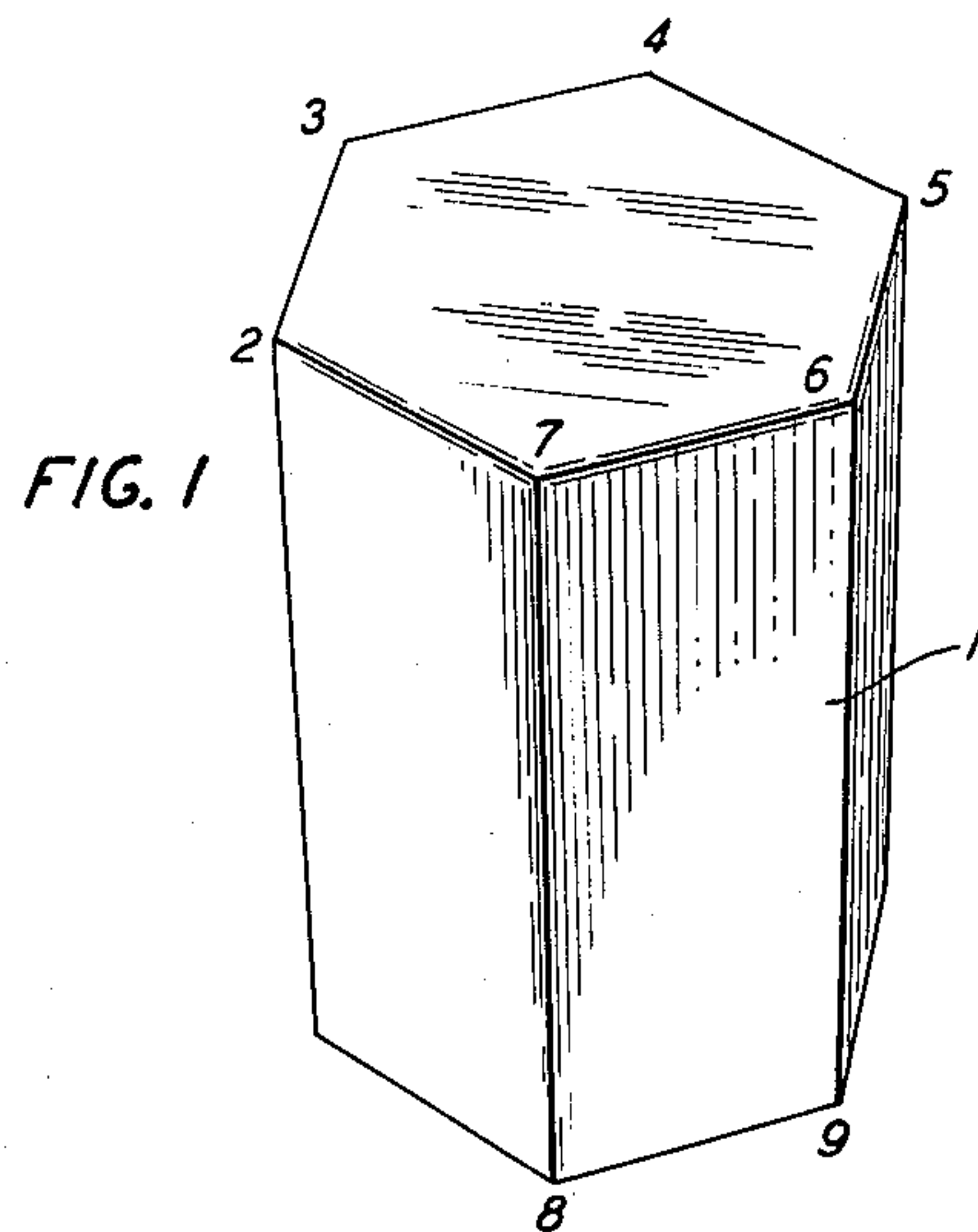
A. A. BALLMAN ETAL

3,234,135

GROWTH OF BERYL CRYSTALS

Filed May 4, 1962

3 Sheets-Sheet 1



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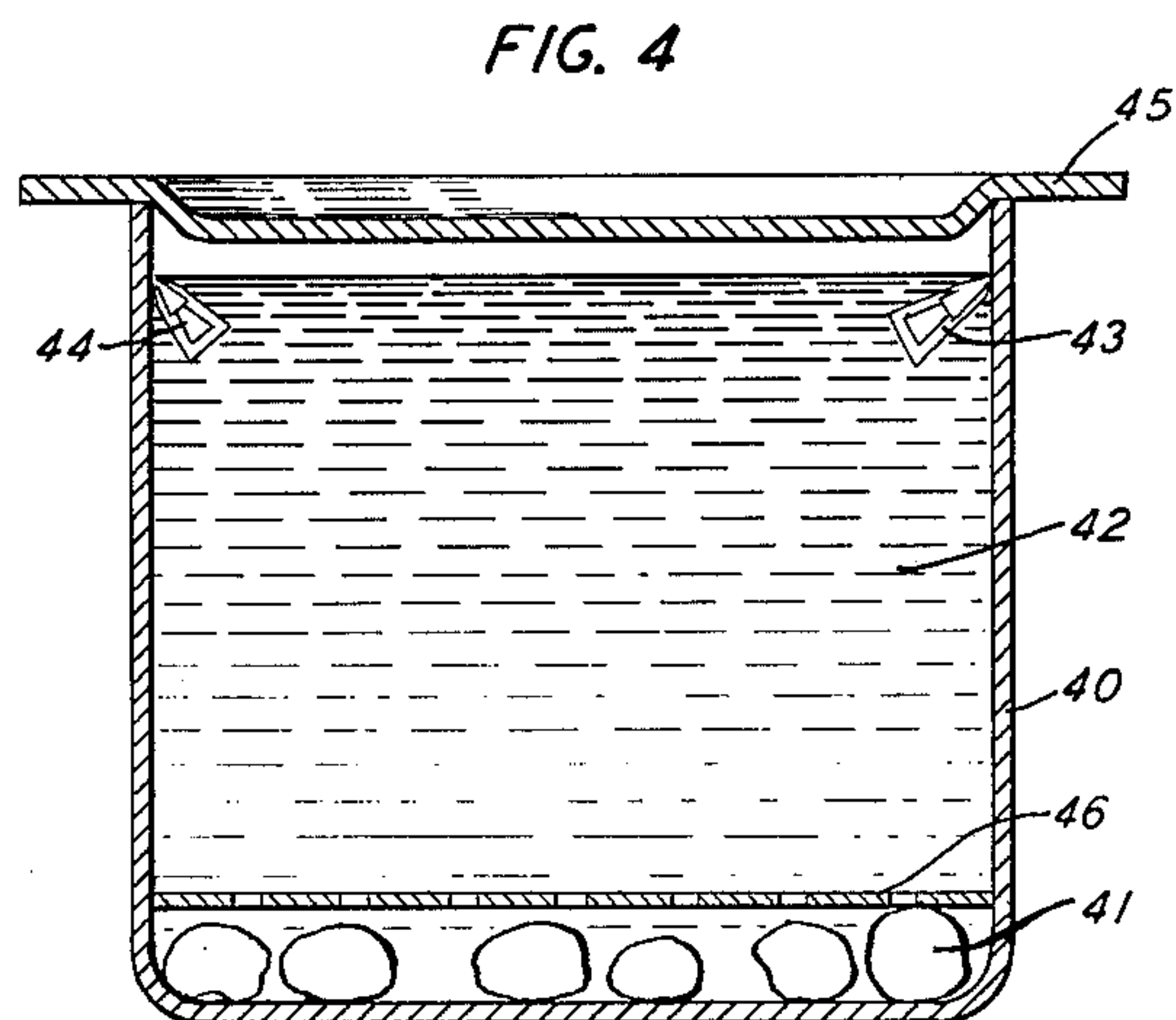
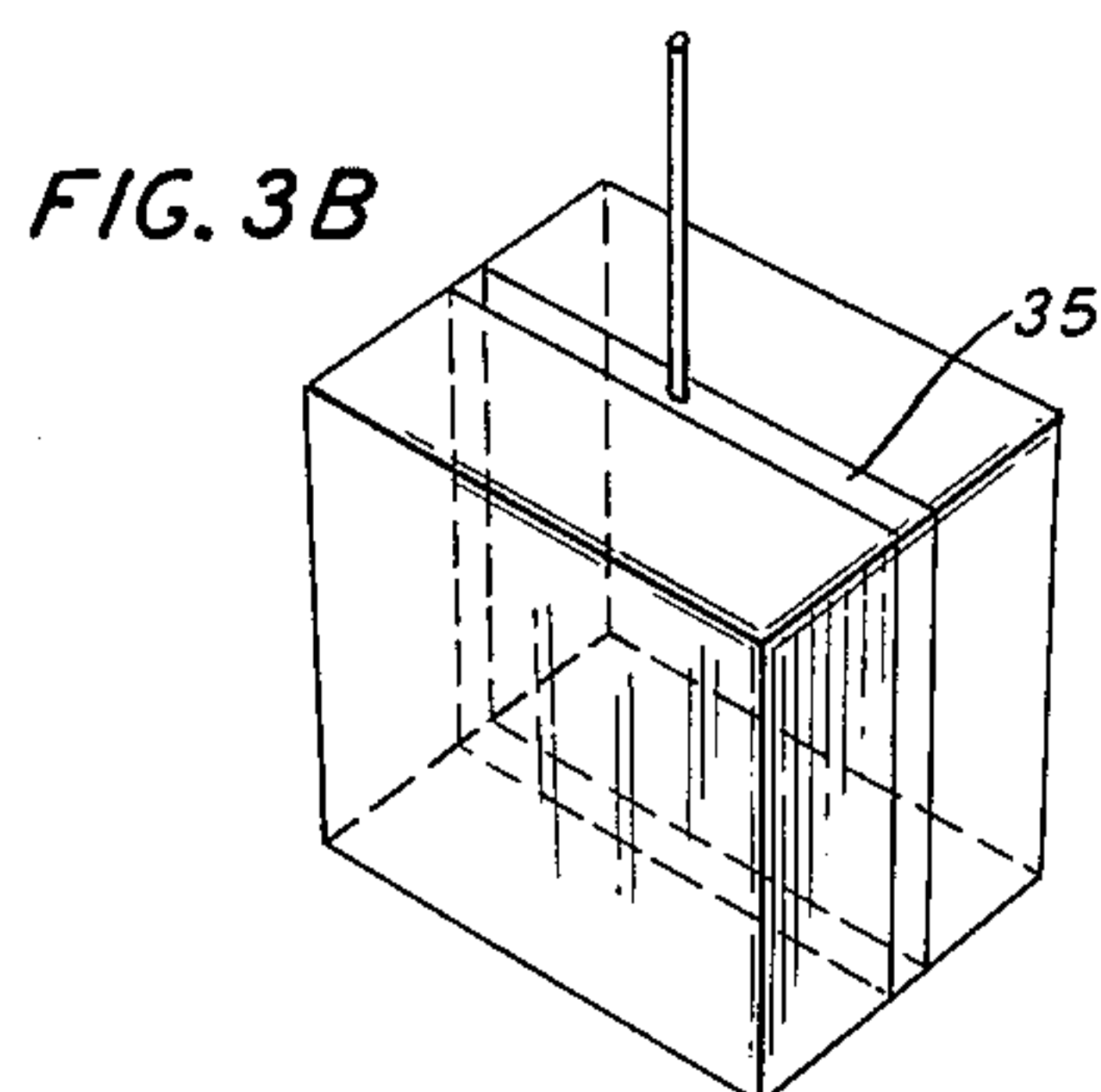
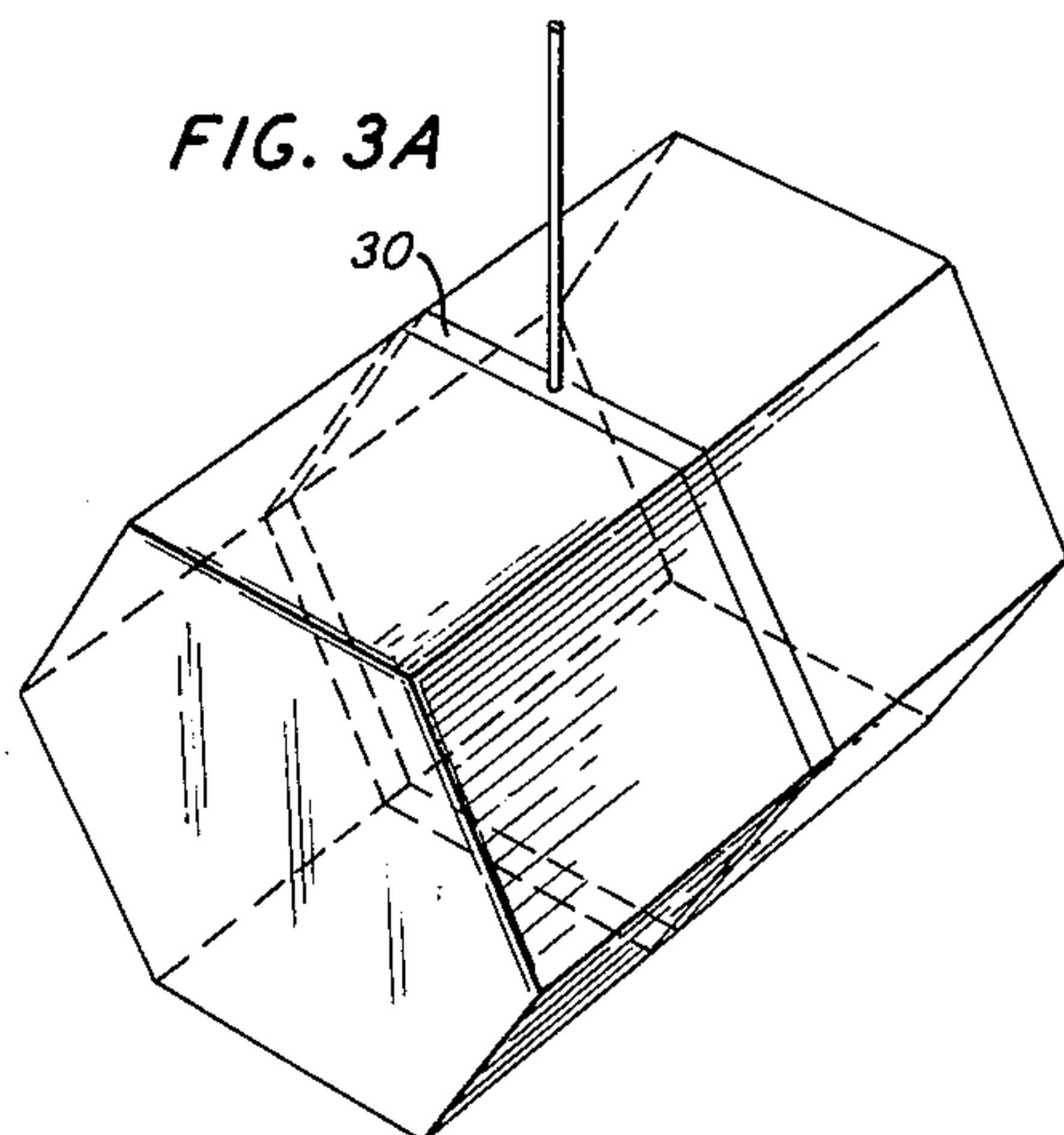
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GROWTH OF BERYL CRYSTALS

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3 Sheets-Sheet 2



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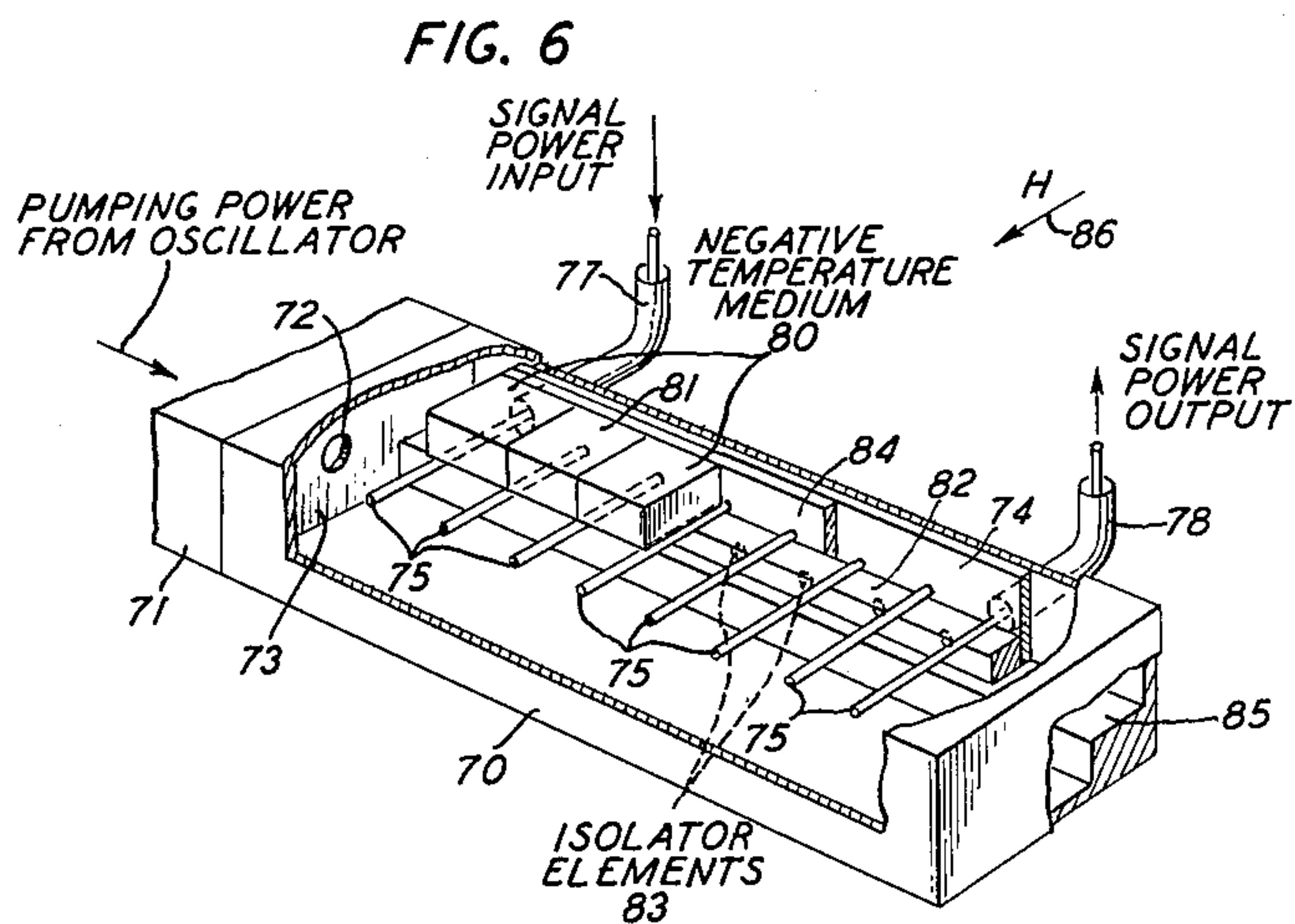
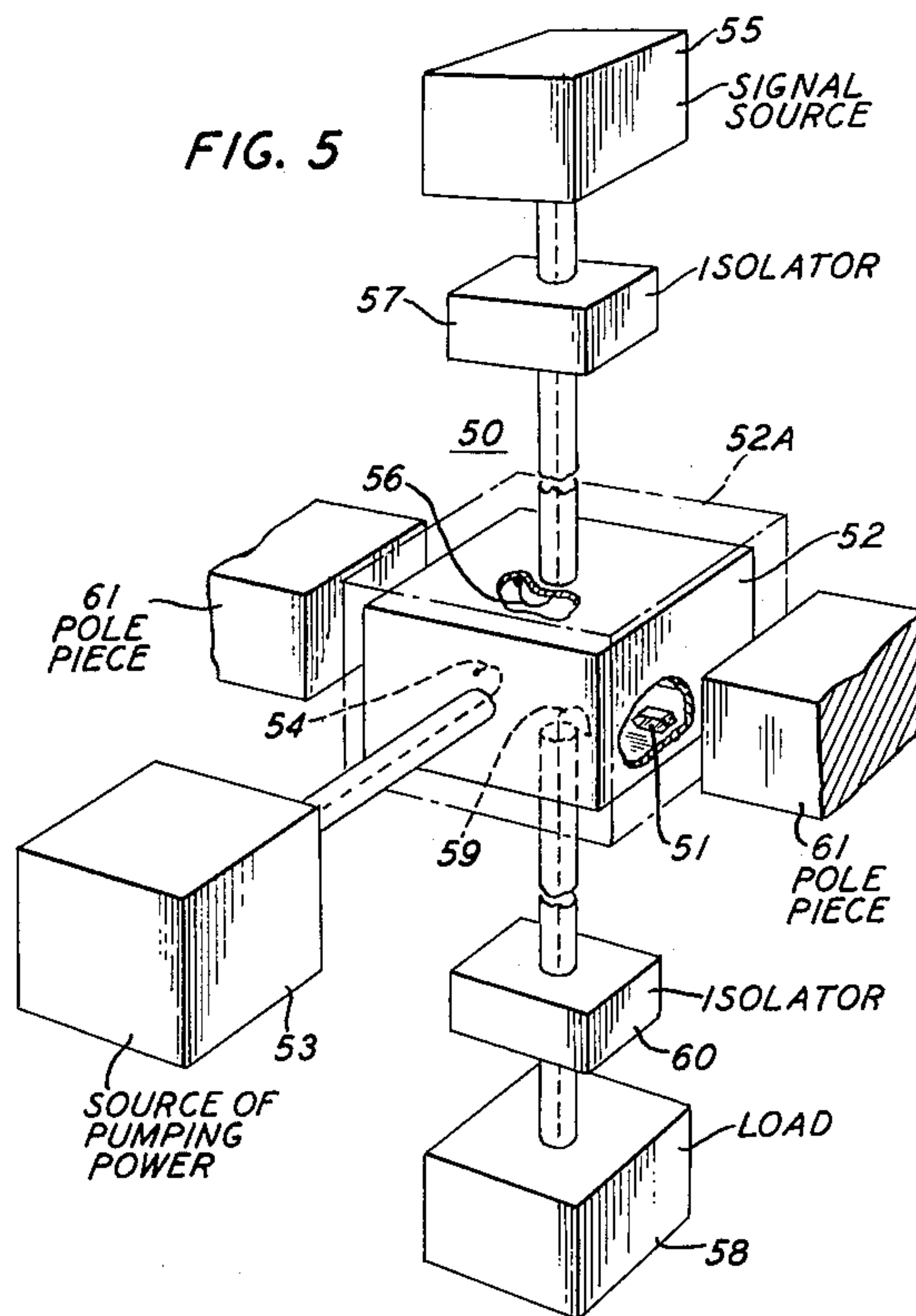
A. A. BALLMAN ETAL

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GROWTH OF BERYL CRYSTALS

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3 Sheets-Sheet 3



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3,234,135

GROWTH OF BERYL CRYSTALS

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16 Claims. (Cl. 252-62.5)

This invention relates to the growth of single crystal-
line beryl ($\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$) by transfer crystallization out
of a flux containing vanadium pentoxide. Crystals grown
in this manner are of interest for electrical applications,
as in microwave masers including those of the cavity or
traveling wave type and as gem stones. In either use,
any of the usual inclusions of interest may be added.

Recent developments in electrical circuit elements such
as parametric amplifiers, transistors, and microwave and
optical masers have stimulated concomitant developments
in the crystal growing arts. Various techniques including
flame fusion, spontaneous and seed nucleation, both from
aqueous and non-aqueous flux, as well as hydrothermal
procedures have in general resulted in the crystallization
of materials suitable for these purposes. Crystalline ma-
terials which are now commercially synthesized include
semi-conductor materials such as silicon, germanium, and
the III-V intermetallic compounds, ferrimagnetic mate-
rials such as yttrium-iron garnet and the various ferrites,
and oxidic materials such as sapphire including various
paramagnetic ions, calcium tungstate, and various molyb-
dates, as well as a host of others. Many of these develop-
ments have resulted, too, in the growth of excellent gem
stone crystals.

Despite this intense interest in such crystalline mate-
rials, however, there is at this time no generally accepted,
commercially feasible system for synthesizing beryl. While
recorded interest in the growth of beryl contain-
ing chromium goes back some seventy years (see P.
Hautefeuille, A. Perrey, 106 Comptes Rendus, 1800
(1888)), and while subsequent literature references sug-
gest the possibility of such synthesis by most of the tech-
niques described above, no general solution has been dis-
closed. Impetus has recently been given to the search
by the wide scale adoption of the microwave maser, par-
ticularly that of the traveling wave type (see United States
Patent 3,004,235). While many such devices containing
ruby elements are in use, it has been found that certain
of the properties of beryl containing chromium suggest
the substitution of this material at least for certain ap-
plications. For example, it has been determined that the
latter material exhibits a higher zero field splitting, so
permitting increased splitting for comparable magnetic
fields and, thus, the attainment of higher operating fre-
quencies, perhaps in the millimeter region. In the gem
stone field, while most natural crystals are easily synthe-
sized by commercially feasible methods, methods for the
production of emeralds and other suitable green-colored
gem stones have not been disclosed.

In accordance with this invention it has been deter-
mined that beryl crystals of a high degree of perfection
with or without inclusions of interest from a microwave
or gem stone standpoint are produced out of a flux con-
taining vanadium pentoxide by a transfer technique. Pre-
ferred embodiments described herein include growth on
selected faces so as to minimize occlusions, and the use
of excess beryllium and aluminum oxides to prevent for-
mation of a glassy face which otherwise may interfere
with crystalline growth. Inclusion of chromium or iron
in varying amounts may result in colored crystals known
to the gem industry as aquamarine, emerald, and mor-

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ganite. Chromium and iron are illustrative of the tri-
valent paramagnetic ions which may be substituted for
aluminum to produce desirable electrical properties.

Description of the invention is expedited by reference
to the drawing, in which:

FIG. 1 is a perspective view of a natural hexagonal
beryl crystal;

FIG. 2 is a cross-sectional view of apparatus suitable
for the growth of beryl by a seed process in accordance
with this invention;

FIG. 3A is a perspective view of a seeded growth pro-
duced on a slice cut normal to the *c*-axis;

FIG. 3B is a perspective view of a seeded growth pro-
duced on a slice cut to include the plane defined by the
c- and *a*-axis;

FIG. 4 is a cross-sectional view of apparatus being used
for spontaneous nucleation by a transfer process herein;

FIG. 5 is a perspective view, partly in section, of a
cavity-type microwave maser including a crystal of beryl
grown in accordance with the instant invention; and

FIG. 6 is a perspective view, partly in section, of a
traveling wave type microwave maser, also containing a
crystal grown in accordance with the processes herein.

Referring again to FIG. 1, there is depicted a crystal
of beryl which represents a typical growth habit. In this
figure, the *c*-axis of the crystal is vertical, defining the
major axis. The upper hexagonal face 2-3-4-5-6-7 nor-
mal to the *c*-axis defines an *a*-plane. Other natural faces,
usually quadrangular in shape, illustrated by 6-7-8-9
occur parallel to the *c*-axis. Such natural faces may rep-
resent a plane defined by the *c*- and *a*-axis or one defined
by the *c*-axis and the direction perpendicular to an *a*-axis
and a *c*-axis. In accordance with this invention, seeded
growth is most advantageously carried out on one of the
three natural faces discussed. In accordance with a pre-
ferred embodiment herein, it is shown that most perfect
growth results from a seed including or parallel to a
natural rectangular face. In discussing such crystal faces,
it is to be understood that reference is had to ideal crystal-
lographic faces. Actual crystals from which seeds are
cut may contain additional capping or other faces.

FIG. 2 depicts a furnace 15 and contained receptacle 16
in which seeded growth in accordance with this invention
is being carried out. While any furnace capable of at-
taining a temperature of the order of 600° C. or any
higher temperature specified herein is suitable for the
practice of this invention, the high evaporation rate of
molten flux material (V_2O_5) 17 and its high rate of reac-
tivity with many materials such as the usual conductive
materials results in a preference for a protective liner
where a resistance type furnace is used. Apparatus found
particularly suitable is that containing a high density
alumina core. Alternatives include Inconel, Mullite, or
other suitable lining materials. In the figure, sectional
member 18 may be considered as representing a cross
section taken through a toroidal core of such a furnace.
Receptacle 16, shown as including seed crystal 19 sus-
pended on hanger 20 and immersed in molten flux 21 and
also containing solid nutrient material 22 is supported
by block 23, which may be a refractory ceramic. While
a vertical temperature gradient from bottom to top within
the flux material 21 is required for the transfer processes
herein, energy is conserved by use of a loosely fitting
lid 24 made of zirconia, alumina, or other suitable ma-
terial. It may be desirable to include a baffle 25 to con-
fine nutrient material 22 and/or to establish a desired tem-
perature gradient.

FIGS. 3A and 3B illustrate two types of seeded growth
which may result by use of the apparatus and process
depicted in FIG. 2. Hexagonal growth, shown in FIG.
3A, results from immersion of a seed crystal 30 including

or parallel to a natural hexagonal face such as 2-3-4-5-6-7 of FIG. 1. It is seen that under these conditions growth is primarily in the *c* direction, the resulting product exhibiting the hexagonal faces typical of the natural habit depicted.

In FIG. 3B, growth resulted from immersion of a seed 35 including or parallel to either of the types of natural quadrangular faces discussed in conjunction with FIG. 1. While, for simplicity, growth is shown primarily in a direction normal to the major faces of seed 35, it is to be recognized that a certain amount of *c* direction growth results so that the actual product manifests some edge growth normal to the minor faces of the seed as well as to the major faces. Such edge growth is at a maximum at the seed and is reduced in the direction of growth normal to the major seed faces.

FIGS. 3A and 3B are not to be construed as restrictive, it being understood that growth results regardless of the orientation of the seed crystal.

FIG. 4 represents a receptacle 40 containing nutrient 41 and flux 42, as herein discussed, but in which growth is proceeding spontaneously so as to result in deposits 43 and 44. Suitable apparatus for such a spontaneous process is identical to those considered in conjunction with the apparatus of FIG. 2, and receptacle 40 may be treated as being enclosed in the furnace there depicted. Since no provision need be made for insertion of a seed, cover lid 45 may be solid, as shown. Again, the use of a baffle such as 46 may be advantageous as discussed in conjunction with FIG. 2.

FIG. 5 depicts a cavity type microwave maser device such as that described in United States Patent 2,981,894. Utilizing the materials grown in accordance with the present invention, such devices, as well as the traveling type counterpart of FIG. 6 are capable of producing oscillation or amplification of microwave energy of wave lengths as high as those in the millimeter range by stimulated emission. While a more complete description of the device appears in the aforesaid patent specification, a brief description is set forth below.

Cavity maser device 50 depends for its operation on beryl crystal 51, which contains one or more paramagnetic ions as discussed herein. Crystal 51 is housed in a cavity resonator 52 which is desirably maintained at operating temperature by a suitable refrigerating apparatus shown schematically by the broken lines 52A. Pumping power of the appropriate frequency is supplied from a local oscillator 53 by way of a coupling loop 54. Input signal power is applied from source 55 by way of coupling loop 56. It is advantageous to include an isolator 57 in the signal path. Output signal power is abstracted from the resonator by load 58 by way of coupling loop 59. A second isolator 60 is shown along the signal path intermediate the load and cavity resonator. Pole pieces 61 are included to achieve the desired field splitting necessary to match the signal frequency.

A traveling wave solid state maser of the type described is described in United States Patent 3,004,225. At this time commercial interest in microwave maser devices is largely centered on the traveling wave device by reason of the larger amplification and other advantages which obtain in common with other slow wave devices. In the figure there is shown a shorted section 70 of a rectangular waveguide so proportioned as to support a standing wave of pumping power, fed from an oscillator not shown, by a waveguide 71 through an iris 72 in one end of wall 73 of section 70. Mounted in a base member 74 and contained by the waveguide section 70 is a spaced parallel array of conductive elements 75 which are orthogonally disposed with respect to the longitudinal axis of the section 70. The elements 75, which are advantageously copper plated tungsten rods, are secured to the base member 74. The end elements of the array 75 are, respectively, the terminal portions of the center conductors of two coaxial transmission lines 77 and 78, line 77

forming an input path for a signal wave to the section 70 and line 78 serving to abstract from the section or amplifying chamber 70 an amplified replica of the signal wave.

The device depends for its operation on a plurality of spaced blocks 80 of a negative temperature material, which in this instance is composed of the synthesized beryl containing one or more paramagnetic ions produced by the invention herein. Blocks 80 are separated by intermediate spacer blocks 81 of a material having a dielectric constant to match that of beryl blocks 80. Such spacer blocks may be composed of beryl, also grown by the process herein but containing no paramagnetic ions. Positioned on the other side (bottom side in FIG. 6) of the array of elements 75 is a bar 82 which manifests a non-reciprocal gyromagnetic rotating effect due either to its own homogeneous properties or to the inclusion of isolator elements such as 83. While in the latter case the gyromagnetic influence is produced by the ferrimagnetic rotation of a material such as yttrium-iron garnet, in the former the influence may result from the paramagnetic rotation effected at low temperature by use of a bar 82 which, again, may be composed of a beryl crystal grown in accordance with the procedures herein. In accordance with such alternative embodiment, it is necessary to regulate the paramagnetic ion inclusion or to misorient the material of bar 82 relative to the orientation of blocks 80 so as to cause bar 82 to act as a positive temperature absorber of reflected signal wave energy rather than as a negative temperature medium (range of from one to five percent is suitable).

The maser structure depends for its operation upon a static magnetic field indicated by arrow 86 parallel to the rods 75 and through the volumes of the blocks 80 and 83 by means of which field both the zero splitting necessary for achieving the required discrete energy levels in the materials of blocks 80 and also the nonreciprocal absorption characteristics of the bar 82 are established.

It is convenient to describe the inventive processes in general terms. This discussion, presented in two parts, the first directed to seeded growth and the second to transfer spontaneous nucleation, is set forth with reference to the apparatus of FIGS. 2 and 4, respectively. Suitable parameter ranges are set forth. Following the general description, specific examples relating to growth of various types of beryl material are listed. Discussion is, for expediency, in terms of V_2O_5 flux although, as discussed, additional material may be present in the flux.

GENERAL DESCRIPTION

Into a platinum or other suitable container, in this illustration of a capacity of 100 cc., are inserted reacted beryl, either natural or synthesized, or in the alternative, the components necessary to produce the composition (e.g., BeO , Al_2O_3 , and SiO_2). To this may be added any paramagnetic ion or other ion inclusion desired, such for example as the chromium and/or iron commonly present in the natural crystals. In the event the components are inserted, the amounts are identical to or approximately those required for the desired stoichiometry. In either event, excess beryllium or aluminum may be included in accordance with a preferred embodiment described herein. For this illustration (100 cc. container), the total amount of beryl or starting components may total approximately 20 grams. As also discussed herein, particularly where the starting material is beryl produced by natural growth or other technique resulting in water inclusion, it may be desired to pretreat such nutrient so as to effectively remove the water content by heating to several hundred degrees centigrade ($500-1000^\circ C.$) for a period sufficient to remove water (from one to several hours). To this there is added a total amount of flux necessary to result in the establishment of a molten path from the nutrient material to the seed. In common with other transfer processes, the amount of the flux finally present is not critical, its only purpose being to serve as a

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transfer path from nutrient to growth position. Since, however, the V_2O_5 is a solvent for the nutrient, the maximum amount of such medium permissible is just short of that which results in total solution. In this illustrative example (four inch high crucible), the amount of V_2O_5 eventually added is that required to cover the seed crystal position (approximately 180 grams of V_2O_5).

Depending on whether the nutrient material is reacted beryl or the starting components, there is a difference in the procedure by which the V_2O_5 is added. In the former situation, it is necessary only to add the total amount of required transfer medium. In the latter, due to the evolution of gases resulting from decomposition of the components, it is recommended that only that amount of V_2O_5 necessary to result in a molten body covering the components be initially added, after which the temperature of the contents of the receptacle is raised so as to melt the transfer media and decompose the components, the temperature then being maintained at such level for a period necessary to decompose the components and react so as to result in formation of the beryl and oxides of any excess components included. After a suitable sintering period (of the order of several hours) following gaseous evolution, the remaining V_2O_5 is added, the additional amount being such as to raise the level to above the position of the seed crystal.

It is next necessary to bring about thermal equilibrium between an inserted seed and the transfer medium. This is accomplished by inserting the seed crystal into the molten V_2O_5 and maintaining the two at temperature. Where this period is to be prolonged and it is desired to dissolve a portion of the surface layer, it may be necessary to use a somewhat thicker crystal. The inserted seed crystal faces will continue to dissolve until the transfer medium has become saturated with respect to beryl in the vicinity of the seed. Where dissolution is to be minimized, the container and contents are maintained at temperature for a prolonged period prior to insertion of the seed. For the illustration discussed, it has been found that a period of several hours is required to produce saturation at the seed crystal position.

In either event, saturation may be accelerated by stirring. A suitable operating temperature range is defined by expediency at the low end; it being found that reasonable growth rates are achieved only with temperatures of the order of 600° C. and higher. A maximum temperature limit is imposed by the tolerable rate of evaporation of the V_2O_5 flux when operating in an open system. From this standpoint, it is recommended that temperatures of appreciably above 1200° C. not be exceeded.

As discussed, nutrient materials may comprise fully reacted beryl, as from a natural or other source, which may or may not contain the paramagnetic ions or other inclusions desired. In addition, the nutrient may consist of any components which will react to yield the desired beryl composition. Illustrative component materials in addition to the elements themselves are beryllium compounds (oxide, nitrate, sulfate, silicate, chloride, et cetera), aluminum compounds (oxide, hydroxide, sulfate, aluminate, nitrate, et cetera), the silicon-containing material (silica, silicic acid, lithium silicate, silicon carbide, silicon oxide, et cetera), together with any other ion-containing material desired. Such additional compounds may include those containing chromium, iron, manganese, et cetera. Amounts of such inclusions are determined by the desired end product, it being kept in mind that only approximately one-half of such material included in the nutrient is eventually included in the growing crystal. Where it is desired to grow gem stone compositions, the amount of ion inclusion in the nutrient is as follows:

Aquamarine—about one-half of one atom percent of chromium based on the aluminum in the crystal (about one percent to be included in the nutrient).

Emerald—amounts ranging up to as high as five atom

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percent of chromium based on the aluminum in the crystal (again of the order of two times this amount is required in the nutrient to result in such crystal composition).

Morganite—from a small fraction up to five atom percent of iron based on the aluminum in the crystal (same excess required in the nutrient).

For microwave applications, where the material is to serve as a negative temperature medium, at least one paramagnetic ion is included in the crystal. An exemplary inclusion is of the order of .5 atom percent, again based on the aluminum in the crystal. The most common paramagnetic ion added for this purpose is, again, chromium. Where it is desired to reduce relaxation time in the product crystal, it has been found that such desiderata may be achieved by the additional inclusion of iron, the order of this inclusion being up to about 3 percent, based on the aluminum in the crystal. Where the product crystal is to serve as a positive temperature absorber rather than a negative temperature medium, larger amounts of paramagnetic ion are conventionally added. Such amounts may range from 3 to 10 atomic percent.

It has been mentioned that seeded growth is desirably carried out from a plane including or parallel to a natural crystal face. While growth may proceed from any orientation, the natural growth habit results in a more uniform product. Most rapid growth in beryl is in the *c* direction, such growth being advantageously produced from a natural hexagonal face or a seed cut parallel to such a face. While growth from a natural quadrangular face or a seed cut parallel to such face is slower, any occlusions are minimized and a more perfect crystal results. Typical growth rates are 30 to 50 mils per day in the *c* direction and 10 to 30 mils per day from a quadrangular seed. For the illustrative process discussed herein, typical seed sections may be of dimensions of the order of 100 mils thick and of any major dimensions which may be accommodated by the receptacle. For this apparatus, crystals have been grown on seeds of the order of 2 inches square. Where the seed is to be inserted in the flux prior to the attainment of saturation at this position, it may be desirable to use thicker sections of the order of perhaps 150 mils or larger. In general, the nature of the nutrient, both as to the aggregate distribution and size, as well as purity, are not critical. It is, however, preferred that the nutrient materials have minimum particle dimensions of the order of 10 mils to permit sintering and to keep the rate of transfer within controllable bounds. Where it is desired to minimize the rate of growth at any particular operating temperature, this may be achieved by increasing particle or aggregate size or by the use of baffles. Where the nutrient material is reacted beryl, it is preferred that particle or aggregate size be no smaller than about 10 mils, again to prevent unduly rapid transfer.

It has been observed that the use of nutrient, whether reacted or components exactly equivalent to the stoichiometric requirements of the end product, results in the initial formation of a certain amount of glassy material of a composition having a high silica content due to the high solubility of beryllium and aluminum. While such formation may be permissible, it is likely to interfere with crystalline growth and may necessitate removal of the seed one or more times during the process. In accordance with the preferred embodiment herein, it has been found that the use of excess beryllium and/or aluminum may eliminate such formation. To this end it has been determined that glass formation is substantially avoided by saturating the solution with respect to both beryllium and aluminum. Exceeding this solubility limit is not harmful and results merely in the precipitation of beryllium and aluminum compounds. It has been observed empirically that excess of both of the concerned elements of the order of one weight percent of

the flux is sufficient to ensure uninterrupted crystalline growth.

The desirability of pretreating the nutrient beryl to remove occluded water has been discussed. The same reasoning dictates a similar pretreatment of the seed crystal where it is sliced from a natural crystal or otherwise contains moisture. In the absence of pretreatment, it is likely that the increased temperature resulting from immersion in the flux causes rapid evolutions of gases, so possibly resulting in strain growth or even in dislocation of the seed crystal. From a practical standpoint, such copious evolution is deleterious. Removal of water may be accomplished by slowly raising the seed to a temperature of the order of about 500° C. or higher and maintaining it at such temperature for a period of several hours. It has been indicated that a temperature range of from 700 to 1200° C. is suitable for the operation of procedures herein. One of the chief advantages, however, of the V_2O_5 flux is the fact that it exhibits a fairly low viscosity and that it can be heated to relatively high temperatures without appreciable dissociation, so permitting a fairly rapid growth rate. Such considerations, together with the desire to minimize loss of materials through evaporation, give rise to a preferred temperature range of from 800 to 1150° C. with optimum conditions being attained at about 1050° C. All of the procedures covered herein are transfer processes. Consequently, rate of growth is dependent not solely on the average or over-all temperature within the receptacle but also on the temperature differential between the position of the nutrient and the position of the seed. In general, it has been found that a minimum differential of the order of 5° C. is required. The desire to maintain an orderly growth mechanism gives rise to a maximum temperature differential of the order of 500° C. Of course, a smaller gradient is permissible where slower growth rates may be tolerated.

The general procedure has been described in terms of seeded growth. The spontaneous transfer procedure of FIG. 4 is carried out in identical fashion except that a seed crystal is not inserted into the flux. All other considerations, including temperature ranges, flux, and nutrient and concentrations, are identical. The spontaneous transfer procedure is facilitated by the fact that the beryl or nutrient components all have a specific density higher than that of the molten flux at the optimum temperature of 1050° C. or higher, so providing a natural separation between this material and the growing crystals. Such separation at lower temperatures can be facilitated by the use of baffles to hold the components down. Baffles may also reduce growth rate and limit the movement of particles by thermal convection. Since spontaneous growth may result in homogeneous crystals manifesting natural faces not dissimilar to those illustrated by FIG. 1, it is this type of growth which may be of primary interest to those concerned with the synthesis of gem stone quality material. While such crystals may be of interest for use in microwave devices, it has been noted that the controlled growth resulting from seeding on a rectangular plane coincident with or parallel to a natural face is of high quality and is most desirable for such applications. In common with other spontaneous nucleation processes, the size and quality of the resultant crystals are strongly dependent upon growth rate, slower rate favoring improvement in both parameters.

The following specific examples illustrate the growth of both seeded and spontaneously nucleated beryl containing various inclusions by the inventive processes. All runs were carried out in a 100 cc. crucible. All seed crystals were pretreated at 500° C. so as to remove water prior to insertion in the flux.

Example 1.—Seed growth of clear beryl without excess BeO or Al_2O_3

30 grams of natural white beryl of an aggregate size

of approximately one-quarter inch are placed in the bottom of the crucible beneath a baffle to which is added 180 grams of V_2O_5 . The crucible and contents are heated to a temperature of approximately 1050° C. over a period of approximately twenty-four hours, after which the cover is removed, and a glassy material which had formed at the surface is removed. Two natural white beryl seed crystals of approximate dimensions 1" x 1" x 100 mils are immersed in the now molten flux, the depth of immersion being sufficient to cover the top of the crystal. The crucible and contents are maintained at the said temperature for about four days. One of the seeds has a hexagonal face; the other, a rectangular. At the end of four days, growth is observed on both flat faces of said crystals. Growth on the first seed (that including a hexagonal face) is of the order of 160 mils on each side; that on the second seed is of the order of 120 mils, also on each side.

Example 2.—Growth of chromium-doped beryl from a flux containing excess beryllium and aluminum

The procedure of Example 1 is carried out, substituting, however, the following components and amounts for the white beryl nutrient:

	Grams
$Be(NO_3)_2 \cdot 3H_2O$ -----	23
$Al(OH)_3$ -----	10
H_2SiO_3 -----	15.6
$NH_4Cr(SO_4)_2$ -----	1

Sixty grams of vanadium pentoxide are inserted. The crucible and contents are raised to a temperature of 1000° C. over a period of approximately two hours and are maintained at this temperature overnight to permit the formation of beryl and other oxides. At the end of this period, 120 grams of V_2O_5 , together with one additional gram of $NH_4Cr(SO_4)_2$, are added, so bringing the level of the flux near the top of the crucible. Two seed crystals, both of natural white beryl, both manifesting natural rectangular faces, and both of approximate dimensions 1" x 1" x 100 mils, are inserted. The crucible and contents are maintained at 1000° C. for four days. Removal of the seeds discloses an emerald-green growth of a thickness of approximately 70 mils on each face of both crystals. Visual examination and microwave measurements disclose the material to be emerald. The grown crystals contain of the order of one atomic percent chromium by weight of the aluminum.

Example 3.—Growth of material of Example 2 with differing starting components

The procedure of Example 2 is repeated, however substituting 3 grams of beryllium oxide for the

$Be(NO_3)_2 \cdot 3H_2O$
and 6 grams of Al_2O_3 for the $Al(OH)_3$. The operating temperature for this example is 1100° C. As in Example 2, glass formation is avoided by the use of excess inclusions of beryllium and aluminum. After removal of the seeds at the termination of the four-day period, emerald growth of the order of 100 mils on each of the four faces is observed.

Example 4.—Seeded growth of morganite

The same type and amounts of starting components are used as in Example 2. In lieu, however, of the inclusion of a chromium-containing compound, there is added 0.3 gram of $Fe(NO_3)_3$. Sixty grams of V_2O_5 are added. Crucible and contents are raised to a temperature of 950° C. over a period of two hours and the said temperature is maintained overnight. At the end of this period, 120 grams of V_2O_5 , together with an additional 2 grams of $Fe(NO_3)_3 \cdot 6H_2O$, are added. The temperature of the contents is maintained at 950° C., again overnight, after which two rectangular seed plates 1" x 1" x 100 mils are inserted. Seed and crucible con-

tents are maintained at a temperature of 950° C. for one week. 75-mil growth of morganite is observed on each of the major exposed faces.

Example 5.—Seeded growth of beryl containing chromium and iron

The initial components are as follows:

	Grams
Be(NO ₃) ₂ ·3H ₂ O	24
Al(OH) ₃	8
H ₂ SiO ₃	15.6
Fe(NO ₃) ₃ ·6H ₂ O	1.25
NH ₄ Cr(SO ₄) ₂	.15

To these starting components there is added 60 grams V₂O₅. Crucible and contents are raised to a temperature of approximately 1000° C. over a period of approximately two hours. Contents are maintained at this temperature overnight, after which 120 grams of V₂O₅, an additional 1.25 grams of the iron-containing compound, and .15 gram of the chromium-containing compound are added. The entirety is again maintained at a temperature of 1000° C. overnight so as to bring the flux to saturation, after which two rectangular seed plates of natural white beryl of approximate dimensions 1" x 1" x 100 mils are inserted. Crucible and contents are maintained at 1000° C. for a period of approximately seven days. Resultant growth is approximately 145 mil thick on each of the four exposed faces.

Example 6.—Growth of beryl containing small amount of chromium

The starting components are:

	Grams
Be(NO ₃) ₂ ·3H ₂ O	24
Al(OH) ₃	8
H ₂ SiO ₃	15.6

Sixty grams of V₂O₅ are added and the receptacle and contents raised to a temperature of 1000° C. in a period of two hours and maintained at this temperature overnight. At the end of this period, an additional 120 grams of V₂O₅ together with 0.3 gram of NH₄Cr(SO₄)₂ is added. Contents are raised to a temperature of 1000° C. and again maintained at that temperature overnight. Natural white beryl slices of approximate dimensions 1" x 1" x 100 mils are inserted, the temperature is raised to 1000° C., and the contents are maintained at such temperature for a period of one week. The resultant growth reaches a thickness of approximately 150 mils on each of the four faces. The material is aquamarine in color. Microwave measurements show a line width of approximately 100 mc.

Example 7.—Beryl and chromium growth by spontaneous nucleation

The procedure of Example 1 is carried out, substituting however the following components and amounts for the white beryl nutrient:

	Grams
Be(NO ₃) ₂ ·3H ₂ O	23
Al(OH) ₃	10
H ₂ SiO ₃	15.6
NH ₄ Cr(SO ₄) ₂	1

Sixty grams of vanadium pentoxide are inserted. The crucible and contents are raised to a temperature of 1000° C. over a period of approximately two hours and are maintained at this temperature overnight to permit the formation of beryl and other oxides. At the end of this period 120 grams of V₂O₅, together with one additional gram of NH₄Cr(SO₄)₂, are added, so bringing the level of the flux near the top of the crucible. The crucible and contents are maintained at 900° C. for two months. At the end of this period the cover is removed. It is observed that natural emerald crystals have formed at the liquid line, such crystals being of dimensions of

up to one carat in size. The grown crystals contain of the order of one atomic percent chromium by weight of the aluminum.

Example 8.—Seed growth of chromium-doped beryl from V₂O₅ additionally containing 7% LiO

30 grams of natural white beryl of an aggregate size of approximately ¼ inch is placed at the bottom of a crucible beneath a baffle having apertures a little smaller than ¼ each to which is added 100 grams of V₂O₅, 7.4 grams of lithium carbonate (representing about 7 percent by weight lithium oxide based on total flux), 0.2 gram of Cr₂O₃, together with 5 grams excess Al₂O₃. The crucible and contents are heated to a temperature of approximately 700° C. over a period of approximately five hours. A beryl seed crystal of approximate dimensions ¼" x ½" x 100 mils is immersed in the molten flux, the depth of immersion being sufficient to cover the top of the crystal. The seed is cut parallel to an *a* face. The inserted seed is rotated during the entire crystallizing process at a rate of approximately 80 r.p.m. The crucible and contents are maintained at the said average temperature for a period of about four days. During this period a gradient ranging from approximately 930° C. in the vicinity of the nutrient down to a low of about 880° C. at the position of the seed crystal is measured. At the end of four days, growth is observed on both flat faces of the crystal. A total growth of about 120 mils (about 60 mils on each face) results.

Example 9.—Seed growth of chromium-doped beryl from V₂O₅ additionally containing 15% LiO

Example 8 is rerun under identical conditions except that the lithium content is increased to about 15 percent (14.8 grams lithium carbonate) together with the same amount of V₂O₅. The growth at the termination of the four-day period is approximately the same as that observed in the preceding example.

It is noted from the examples above that widely varying amounts of excess beryllium and/or aluminum are adequate in ensuring the absence of glassy growth. In certain of the examples where paramagnetic ions were included, such inclusions were made in two parts, one part being made initially and one part together with the final quantity of flux material. Where such inclusions are to be made, this procedure is considered to be preferred since it ensures replenishment of such ion during crystal growth, so resulting in more uniform doping. For expediency, the invention has been described in terms of a limited number of specific embodiments. Such embodiments were selected so as to differ one from the other in simple fashion. Many variations are possible and may be preferred. It is to be understood, for example, that the amount of V₂O₅ is not critical, it being required only that there be sufficient flux to provide a liquid path from nutrient to seed position or, in the alternative, from nutrient to a position of sufficiently reduced temperature to result in spontaneous nucleation, and that the amount of flux be insufficient to result in excessive solution of nutrient material. Where growth on but a single face of the seed is desired the path need include only such face. For seeded growth, the dimensions of the seed plate are limited largely by the size of the container. The apparatus utilized in many of the specific examples was conveniently operated with two seed crystals. Growth proceeds at substantially identical rates on a greater number of immersed seeds providing they are spaced at reasonable intervals.

The apparatus utilized in many of the examples was such as to result in a temperature gradient of the order of approximately 40° C. Smaller gradients are operative, however, resulting in a reduction in growth rate. Higher gradients may be tolerated. The absolute maximum imposed is set by the permissible maximum and minimum temperatures set forth above. It is feasible to operate

with a gradient of 500° C. from a hot temperature of 1200° C. to a cold temperature of 700° C. However, establishment of such a gradient would necessitate the use of a considerably deeper container than that discussed.

It is evident that the growth process proceeds generally without regard to intentional or unintentional inclusions. For certain of the purposes herein it is desirable to include varying amounts of chromium and/or iron as well as other trivalent ions. Other experimental work indicates that relatively large inclusions of other materials may be tolerated in the flux. For example, it has been found that inclusions of the order of 20 weight percent based on the total flux of oxides of such diverse materials as lithium, lead, molybdenum, tungsten, et cetera have little or no discernible effect on the resulting beryl crystals. Since the processes herein are all based on a transfer mechanism and since, as a consequence, the amount of nutrient material in solution at any given time is not a critical factor, flux variations may be made generally without regard to the effect on solubility. In fact, one purpose for varying the flux composition from pure V_2O_5 is to deliberately reduce solubility so as to decrease the rate of crystallization.

Inclusions of such materials made primarily to alter the solubility of the flux and so to vary the rate of crystallization may be made in amounts exceeding such limit.

While, as discussed in the preceding paragraph, broad deviations from pure V_2O_5 flux may be made with impunity where the added materials contain ions of such valence or dimensions as not to appear in the final crystals, it is considered that additions of trivalent ions other than Al^{3+} of nature such as to appear in the final composition should be made in amounts such as to result in a maximum inclusion of the crystals of the order of five percent by weight based on the entire crystal composition.

Variations in the growth procedures are evident. For example, it was noted in Example 1 that it was feasible to use a baffle to help fix the position and differential of temperature gradient, much in the manner that such an element is utilized in a hydrothermal growth procedure. All examples were carried out in air at atmospheric pressure. Other oxygen-containing atmospheres may be substituted. Increasing pressure, while probably not feasible from a commercial standpoint, excellent results being obtainable without the need for additional equipment, results in increasing solubility and, consequently, increasing rate of crystallization.

What is claimed is:

1. Process for the crystallizing of a material consisting essentially of $Be_3Al_2Si_6O_{18}$ by a transfer mechanism in a molten flux consisting essentially of V_2O_5 , comprising heating the said flux together with a solid nutrient selected from the group consisting of $Be_3Al_2Si_6O_{18}$ and reactants capable of yielding $Be_3Al_2Si_6O_{18}$ so as to produce a temperature gradient of at least 5° C. from a minimum value of 700° C., the position of crystallization being kept at said minimum value and the position of the solid nutrient being kept at a temperature at least 5° C. higher than the said minimum.

2. Process of claim 1 in which crystallizing is caused to proceed on an immersed surface of an inserted seed of single crystalline material comprising $Be_3Al_2Si_6O_{18}$.

3. Process of claim 1 in which the said nutrient comprises $Be_3Al_2Si_6O_{18}$.

4. Process of claim 1 in which the said nutrient comprises component materials which react to yield crystalline material consisting essentially of $Be_3Al_2Si_6O_{18}$.

5. Process of claim 1 in which the said nutrient includes an excess of at least one element selected from the group consisting of beryllium and aluminum with reference to the amount of said element required to produce the stoichiometry of $Be_3Al_2Si_6O_{18}$.

6. Process of claim 5 in which the said element is chemically combined.

7. Process of claim 5 in which an excess of both of said elements is included in the nutrient.

8. Process of claim 1 in which the said flux is at least 80 percent by weight V_2O_5 .

9. Process of claim 8 in which the said flux contains up to 20 weight percent of lithium oxide.

10. Process of claim 1 in which the composition of said nutrient is such as to yield a crystalline material containing at least one additional trivalent ion in a maximum amount of 5 percent by weight based on the said crystalline material.

11. Process of claim 9 in which the said trivalent ion is selected from the group consisting of chromium and iron.

12. Process of claim 11 in which the composition of the nutrient is such as to result in a crystal containing both trivalent chromium and trivalent iron, the total amount of such inclusions being a maximum of 5 percent based on the weight of the said crystalline material.

13. Process of claim 1 in which the crystallizing is caused to proceed on an immersed seed comprising $Be_3Al_2Si_6O_{18}$, the said seed having at least one major face approximately parallel to a natural quadrangular face of a crystal exhibiting a hexagonal habit.

14. Process of claim 13 in which the said major face corresponds to said natural quadrangular face.

15. Process of claim 1 in which the crystallizing is caused to proceed on an immersed seed comprising $Be_3Al_2Si_6O_{18}$, the said seed having at least one major face approximately normal to a c-axis of a crystal exhibiting a natural hexagonal habit.

16. Process in accordance with claim 1 in which the crystallizing is caused to proceed on a surface of an immersed seed comprising $Be_3Al_2Si_6O_{18}$ in which the said seed is heated to a temperature of at least 500° C. prior to immersion.

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