

Oct. 18, 1949.

A. N. HOLDEN

2,484,829

CRYSTAL GROWING APPARATUS

Filed June 11, 1945

5 Sheets-Sheet 1

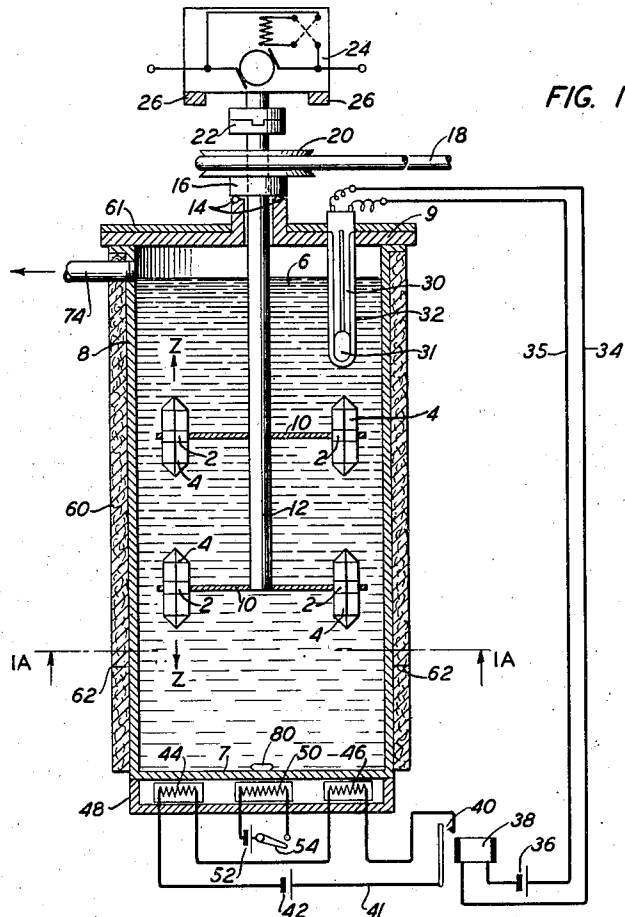


FIG. 1

FIG. 1A

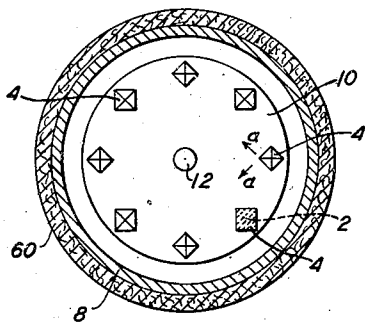
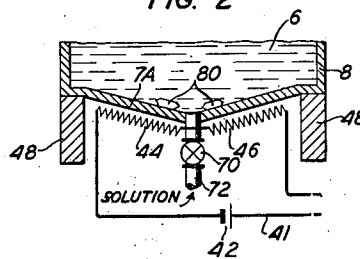


FIG. 2



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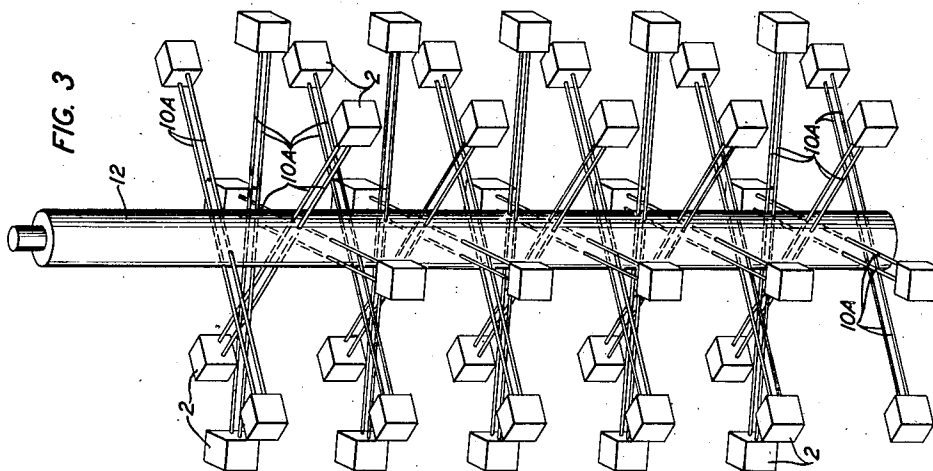
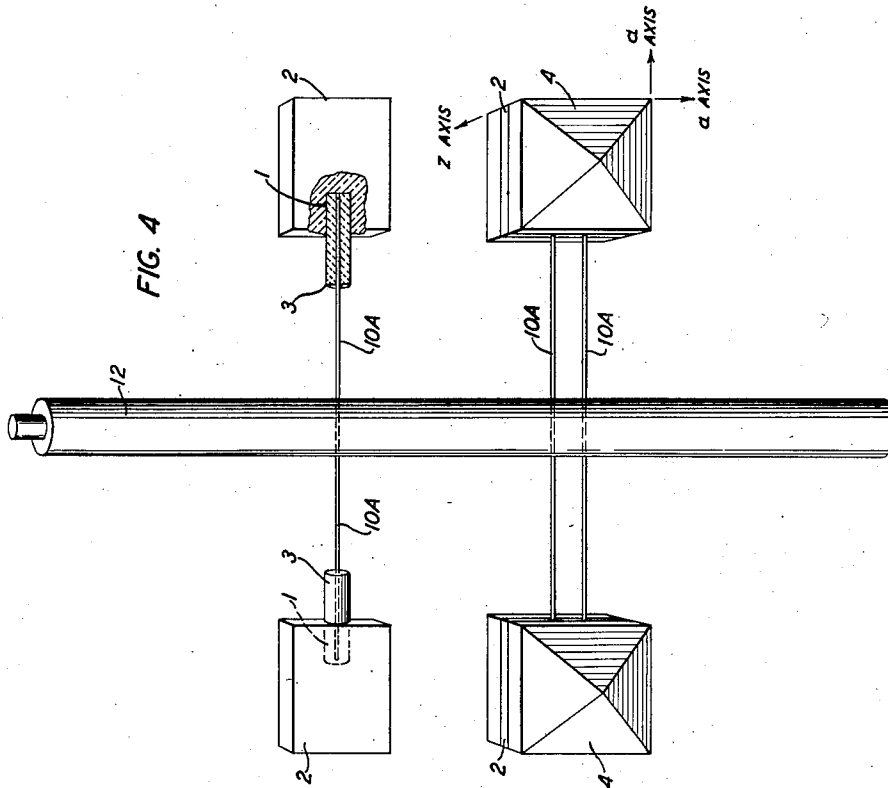
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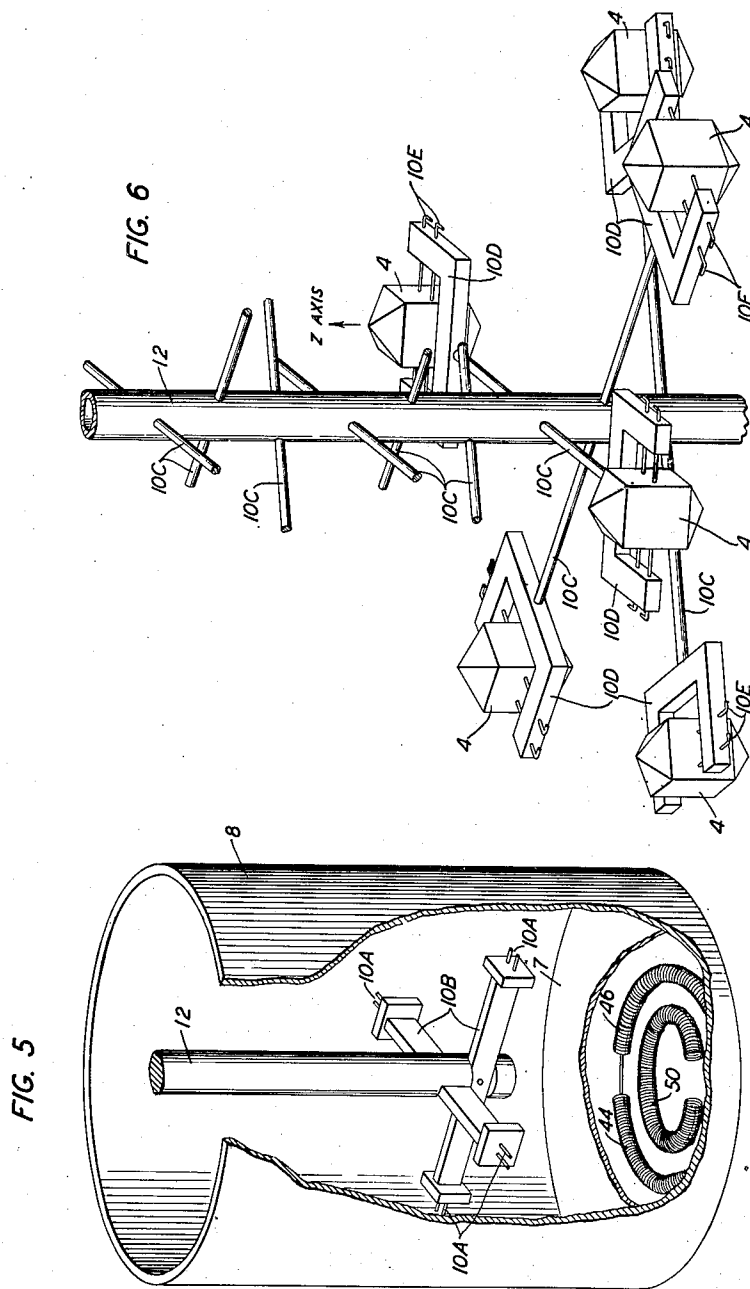
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5 Sheets-Sheet 3



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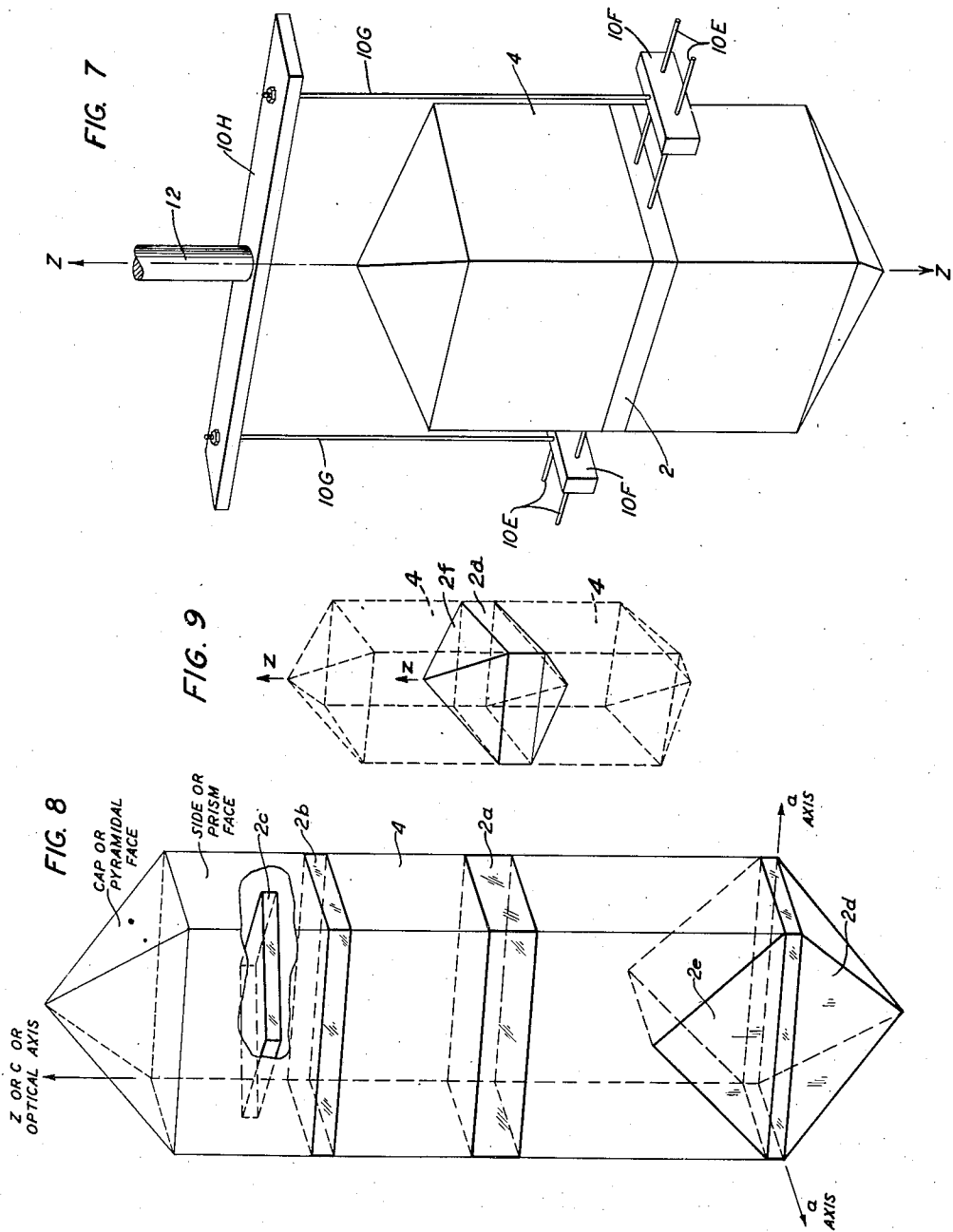
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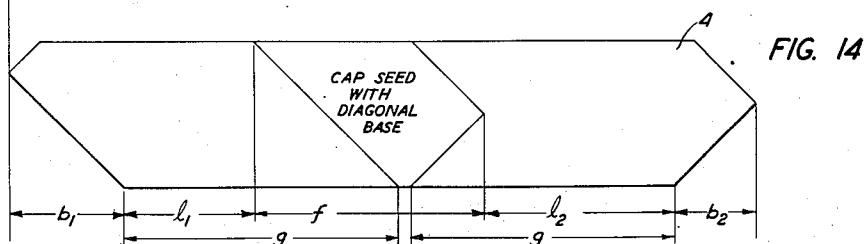
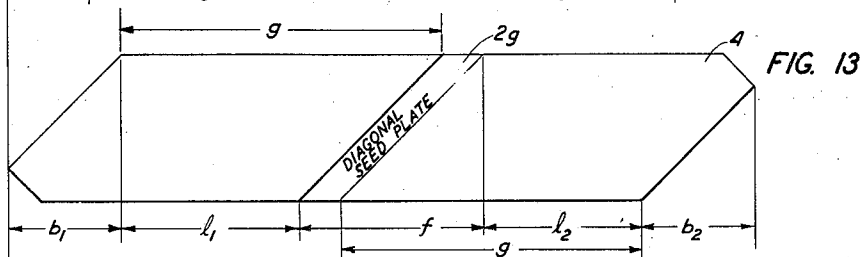
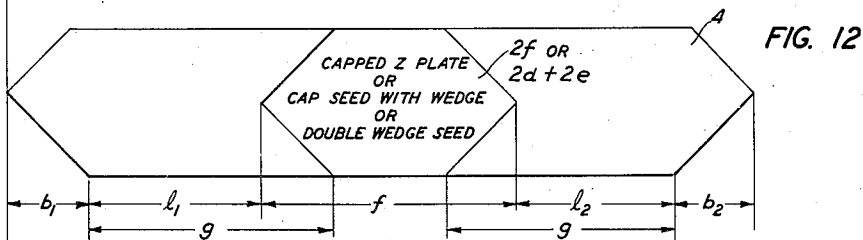
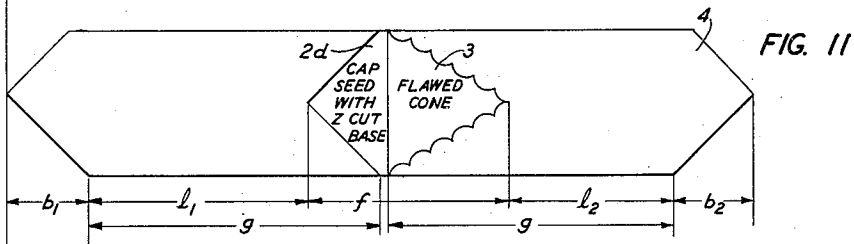
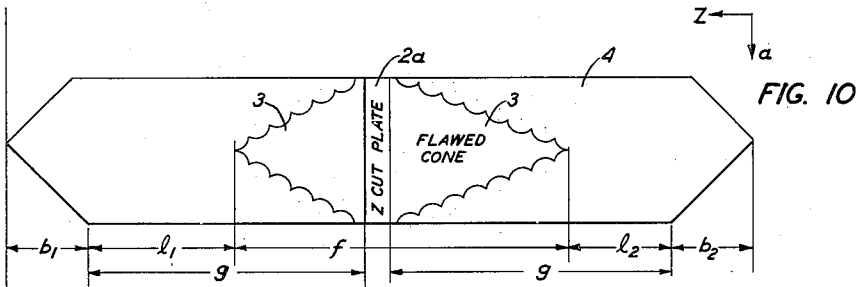
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UNITED STATES PATENT OFFICE

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CRYSTAL GROWING APPARATUS

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6 Claims. (Cl. 23—273)

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This invention relates to apparatus for growing crystals and particularly to crystallizers of the reciprocating or reversing rotary gyrator type which may be used for growing piezoelectric ammonium dihydrogen phosphate crystals and many other types of crystals from a suitable nutrient solution.

One of the objects of this invention is to grow piezoelectric crystals more rapidly.

Another object of this invention is to concentrate and destroy extraneous or spurious seeds in the nutrient solution.

Another object of this invention is to improve the capping of seed crystals used for growing crystal bars.

Among the factors involved in the practical growing of crystals from a nutrient solution are the preparation of the nutrient solution, the preparation of the seed crystals, and the manner of growing the full size crystals from the smaller seed crystals.

In accordance with one feature of this invention seed crystals or other crystals to be grown from a suitable nutrient solution may be carried in contact with the nutrient solution by supports such as by one or more radial arms attached to and carried by a reciprocating rotatable gyrator shaft. The gyrator shaft may be caused to rotate and to reverse its direction of rotation periodically by any suitable means, such as for example, by a reversing motor, a belt or by other reciprocating mechanism capable of driving the gyrator shaft first in one direction of rotation which may be for a number of turns, and then in the opposite direction of rotation which may be for the same or other number of turns. The speed of rotation of the gyrator shaft and the rate of reversal of its direction of rotation may be adjusted to provide the optimum circulation of the nutrient solution relative to the growing faces of the crystals. With this arrangement, the crystals may be grown uniformly and relatively rapidly due to the good circulation of the solution relative to all growing faces of all the crystals carried by the reciprocating rotary gyrator.

The rate at which the unflawed crystal material may be grown is a function of the flow of the nutrient solution past the growing surfaces. This flow may be increased with an increase in the rotation velocity of the gyrator and also by a more frequent reversal of the direction of its rotation. However, as the flow is increased, the turbulence of the nutrient solution is also increased which may in turn increase the likelihood

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for undesired spontaneous seeding of the supersaturated nutrient solution. Accordingly, the most favorable rotational velocity is the highest possible without causing undue spontaneous seeding to appear in the nutrient solution. The optimum flow or circulating conditions depend partly upon the size and the type of mounting used with the growing crystals. The reciprocating action of the gyrator is utilized to obtain a more satisfactory circulation of the nutrient solution with respect to all of the surfaces of the growing crystal, since in cases where the circulation is continuous in one direction only, the crystal may grow imperfectly on the rear surfaces that are trailing in the solution. Furthermore, when the circulation is continuous in one direction only, the crystals, acting as baffles in the solution, tend to propel it with their own velocity and thus the circulation of the solution relative to the crystals declines with increasing time. To obtain favorable flow of nutrient solution over all growing surfaces of the crystal, the crystal may be actuated to turn about its own or other axis by any suitable mechanical means.

Loose extraneous seed crystals in the nutrient solution may, if too numerous, interfere with the growing of the desired crystals mounted on the gyrator. In accordance with another feature of this invention, such loose extraneous or spurious seed crystals formed in the nutrient solution may be concentrated or gathered together in one place and there redissolved into the nutrient solution. Due to the rotary action of the gyrator the nutrient solution is caused to revolve in a circular path, thereby creating a central vortex in the nutrient solution which in turn causes any such loose extraneous seed crystals in the solution to gather and bunch at the central bottom portion of the stationary tank containing the nutrient solution. Heat supplied at such central bottom portion of the container by electrically heated resistors, for example, may be utilized at a suitable temperature to unsaturate the nutrient solution in that particular bottom region only, and thereby cause the loose extraneous seed crystals there bunched by the solution vortex to redissolve into the nutrient solution. As a result of the vortex action in the solution produced by the rotary gyrator combined with the bottom heating action referred to, a supersaturated nutrient solution may be used in the container without interference from loose extraneous seed crystals.

The reciprocating rotatable type of crystallizer is useful in growing large crystals, is inexpensive

to construct, is simple in control and operation, is reliable in results if dependable control and actuating equipment is used in its construction, and the results of the crystal growing process are easily observable at all stages. It has the ability to destroy spurious and spontaneous seeds in the nutrient solution by moving them to the center of the bottom of the tank and there dissolving them. It uses large compact volumes of solution which are more stable with respect to spontaneous seeding than are small volumes or very shallow depths or layers of the solution. This is probably because the stability of supersaturated solutions is associated with thermal inertia effects. Where small quantities or volumes of supersaturated solution are used in thin layers, the thermal inertia thereof is relatively small, and as a result relatively small fluctuations in the ambient temperature conditions may so disturb the conditions of the solution in limited regions that considerable spontaneous seeding may occur therein, a condition that does not occur in a relatively larger volume of the supersaturated solution. For example, in the known rocking tank type of construction, a thin layer of solution is distributed over the upper inside wall of the rocking tank at each swing thereof, and extraneous seeding may readily take place there by evaporation if there is a small vapor leak or an unsuitable temperature gradient surrounding the tank. This condition is absent in the reciprocating rotatable type of equipment involved in this invention where large compact volumes of solution are used, and where the circulation of the growing crystal with respect to the solution is accomplished with a minimum of disturbance to the supersaturated solution. In the equipment of this invention, the power required to accomplish the circulation of the solution with respect to the growing crystal is comparatively small and the circulation is comparatively very uniform with respect to all of the growing crystals in the tank. While the rate at which a crystal can be grown is an increasing function of the relative velocity between the growing crystal surfaces and the supersaturated solution supplying the nutrient salt, this velocity may not be increased indefinitely without creating turbulence violent enough to cause spontaneous seeding, but a much greater relative velocity between the growing crystal and the solution may be attained by this invention without suffering the results of spontaneous seeding in the solution. This is probably due in part to the method here used of establishing the relative velocity, by confining the relative motions principally to the crystal surfaces, and in part to redissolving the spontaneously formed seeds in the central vortex of the solution.

For a clearer understanding of the nature of this invention and the additional advantages, features and objects thereof, reference is made to the following description taken in connection with the accompanying drawing, in which like reference characters represent like or similar parts and in which:

Fig. 1 is a sectional view of a reciprocating rotary gyrator type crystallizer, constructed in accordance with this invention;

Fig. 1A is a sectional view taken on the line 1A—1A of Fig. 1;

Fig. 2 is a sectional view illustrating a modification in the form of the container that may be used in place of the container of Fig. 1, the bottom of the container shown in Fig. 2 being cone-shaped;

Figs. 3 to 7 are perspective views illustrating

various modifications in the form of the gyrator arrangement that may be used in place of the gyrator arrangement of Fig. 1;

Fig. 8 is a perspective view illustrating various types of crystals that may be cut from a crystal bar such as of ammonium dihydrogen phosphate;

Fig. 9 is a perspective view illustrating a capped Z-cut plate seed crystal of ammonium dihydrogen phosphate; and

Figs. 10 to 14 are side views of crystal bars of ammonium dihydrogen phosphate grown from various types of seed crystals.

Referring to the drawing, Fig. 1 is a view in section of a reciprocating rotary type crystallizer useful for growing planted-seed crystals 2 to larger sized crystals 4 from a saturated or supersaturated nutrient solution 6, which is contained in a glass or metal jar, tank or other suitable container 8. The container 8, as illustrated in Fig. 1, is comprised of cylindrical walls, has a flat or nearly flat bottom portion 7, and is provided with a suitable cover 9. The plurality of seed crystals 2 to be grown are carried in full or in partial contact with the nutrient solution 6 by means of one or more radial type supports 10 which are secured to a centrally located and vertically disposed gyrator shaft 12, the upper portion of which may extend through a central opening in the container cover 9 and which may be carried as a whole by a suitable bearing 14, such as the ball bearing 14 and flange 16. The rotary gyrator shaft 12 may be driven by any suitable driver such as a belt 18 and pulley 20 arrangement; or through a clutch 22 by a suitable reciprocating or reversing electric motor 24 which may be carried by a suitable support frame 26. It will be understood that the gyrator shaft 12 may be driven by the reversing motor assembly 24 when carried by the tank cover 9 or by the separate frame 26, and may be geared or otherwise coupled to the gyrator shaft 12 so that the shaft 12 rotates at a suitable speed such as four revolutions per minute or more, and the direction of rotation is reversed every one, two or more revolutions as desired. The power capacity required of the motor 24 is sufficient to overcome the viscous drag effect of the growing crystals 4 through the nutrient solution 6. The ball bearing mounting 14 may be used when it is desired to reduce friction at points where the gyrator 12 is hung.

The temperature of the nutrient solution 6 may be automatically regulated by a suitable thermostat 30 extending through the cover 9 or through any other portion of the container 8 into the solution 6. The thermostat 30 may be connected by conductive wires 34 and 35 with a suitable power supply source or battery 36 for operating a relay 38 having a contact 40 which is connected in a circuit 41 with a suitable power or battery source 42 adapted for heating the resistors 44 and 46. The resistors 44 and 46 are mounted in a base portion 48 which is provided at or along the bottom 7 of the container 8. An additional resistor 50 may be heated by a suitable supply or battery source 52 and may be energized continuously or intermittently by a switch 54. In order to conserve heat supplied by the heating resistors 44, 46 and 50 to the nutrient solution 6 and to provide a more uniform temperature gradient for the nutrient solution 6, a band or girdle 60 composed of felt or other suitable heat insulating material may surround the bottom portion below the region 62 of the outer side walls of the container 8, or may surround the

entire outer side walls thereof. Also, the cover 9 may be covered with a layer of felt 61 in order to control the temperature gradient and distribution of heat from the top to the bottom of the nutrient solution 6.

The container 8 may be a stainless steel tank or a glass jar, such as one made of "Pyrex" glass or other suitable material which is capable of withstanding a considerable amount of heat applied by the resistors 44, 46 and 50 at the bottom 7 thereof, and also which has no unfavorable chemical reaction with the nutrient solution 6. The container 8 is preferably of cylindrical form, and may have any suitable diameter and height, such as for example, a diameter of 12 inches and upwards as desired, or with larger diameters such as 36 inches and much larger. The tank 8 may be closed at its top with a cover 9 made of glass or metal or other suitable material which may be held against a soft rubber or "neoprene" gasket with a suitable clamp. The lid or cover 9 may be sealed tight by tape, if desired. For cold weather operation and for high solution temperatures, the sides of the tank 8 may be protected with a girdle of thick felt 60. The head and closure 9 for the tank 8 may consist of a stainless steel cover plate 9 provided with the bearing 14 for holding the gyrator 12. The small motor 24 with its reversing mechanism may be geared or otherwise coupled to the gyrator shaft 12.

Depending on the size of the tank 8 and the number of radial supports or arms 10 used therein, a large number of crystals 4 may be grown simultaneously in a single tank 8. A considerable number of tanks 8 may be arranged and operated in bank either separately, or together by means of any suitable mechanism such as the pulley and belt arrangement 18 and 20.

The base 48 for the tank 8 may be made of any suitable heat-resistant material and the heaters 44, 46 and 50 enclosed therein may be any suitable heaters such as resistance wire coils. The heaters 44 and 46 may have a heat energy capacity which is low relative to that of the nutrient solution 6 in order to keep the temperature fluctuation of the solution 6 caused by the thermostat controlled heaters 44 and 46 within small and tolerable limits. One or more heaters 44, 46 and 50 may be used. Where a single heater 44, 46 is used, it may be so constructed and located that the center of the bottom 7 of the container 8 receives the more intense heating relative to the heating supplied at the periphery of bottom 7 of the container 8. Where two heaters are used, one heater, such as the heater 50, may be located at the center of the bottom 7 of the container 8 and energized continuously until the temperature approaches so close to the ambient temperature that this constant heat input is no longer permissible, and the other heater such as the resistors 44 and 46 may be located concentrically with the first heater 50 and energized intermittently as is required to maintain the desired temperature of the nutrient solution 6. If the ambient temperature is too low or the temperature of the solution 6 is too far removed from the ambient temperature, heat losses may be prevented or reduced by a girdle of felt 60 of suitable size surrounding the container 8 in order to minimize the heat loss.

The automatic heat control and temperature regulating equipment may comprise any suitable type of thermoregulator 30 and relay 38. The thermoregulator 30 may be inserted in a glass well

32 which has enough liquid to cover the mercury bulb 31 of the thermoregulator 30. The thermoregulator 30 may be, for example, of the standard mercury in glass type, connected so as to operate one or more of the heaters 44, 46 and 50 through any suitable relay 38. The temperature sensitive end 31 of the thermoregulator 30 is inserted in the glass tube 32 which may be held in an opening in the cover 9 by means of a rubber stopper. The glass tube 32 extends into the nutrient solution 6 sufficiently to enable the temperature sensitive element 31 to have proper thermal contact with the nutrient solution 6. Water may be placed in the bottom of the glass tube 32 in just sufficient quantity to make contact with the temperature sensitive regions 31 of the instrument 30 inserted therein, but not enough to produce cooling due to evaporation of the water into the ambient atmosphere. A small piece of sponge rubber may be placed in the bottom of the thermoregulator well 32 to prevent breakage of the mercury bulb 31 of the thermoregulator 30.

While a particular form of temperature control system has been described, it will be understood that any suitable temperature control equipment may be used that is dependable in operation over a continuous growing period which may be in some cases of the order of several weeks, such as six weeks. Temperature control in crystal growing is important since a single temperature fluctuation of excessive amount may result in loss of the run because of flaws that may be introduced into the growing crystals 4. A continuous program of uniform temperature control increments is ideal and requires good temperature control equipment. It will be understood that the container 8 may be placed in a temperature-controlled room, and close temperature control of the nutrient solution 6 may be obtained by means of any suitable and reliable regulator system the temperature control of which may be reliably adjusted to the desired temperatures.

The general principle for growing the crystals 4 involves circulating past the growing surfaces thereof a supersaturated nutrient solution 6, which in the present instance may be mainly primary ammonium phosphate the chemical synonym for which is ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), and slowly lowering the temperature of the nutrient solution 6 in order to keep it in saturated or supersaturated condition. Since the growing crystals 4 continuously remove the nutrient salt from the solution 6, this loss in salt may be continuously compensated for by the decreasing solubility of the salt that results from the decreasing temperature of the nutrient solution 6. Or, instead of employing a decreasing temperature growing schedule to maintain the nutrient solution 6 in saturated or supersaturated condition, the nutrient solution 6 may be adapted to a constant temperature (isothermal) growing schedule at a suitable specific temperature by causing the supersaturated solution 6 to flow continuously through the container tank 8. For this purpose, a suitable pump (not shown) may be used to deliver the clear nutrient solution 6 to the bottom region of the tank 8 through a valve 70 and inlet pipe 72 located in or near the bottom 7A of the tank 8 as shown in Fig. 2, and the spent solution may flow from an outlet pipe 74 as shown in Fig. 1, which may be located near the top of the tank 8, and thence to a saturator (not shown), maintained at a higher temperature than the crystallizer, where the

spent nutrient solution is resaturated, before being returned to the inlet pipe 72. Connecting apparatus provided between the inlet and outlet pipes 72 and 74 may be heat insulated in order to prevent spurious seeding in the circulating nutrient solution, and may be provided with suitable filters (not shown) for cleansing the spent solution from the outlet pipe 74 before redelivering it to the inlet pipe 72.

The reciprocating rotary gyrator shaft 12 may be mounted coaxially with the cylindrical tank 8, and may consist of a stainless steel rod or pipe or a methyl methacrylate resin rod or other suitable material which may be of any suitable diameter such as of the order of 1 inch or more in diameter. To the shaft 12 there may be attached a number of suitable radial type or other type supports 10 on which the seeds 2 and growing crystals 4 are mounted. The supports 10 may take various forms depending upon the size and number of crystals 4 to be grown, and the size of the tank 8 that is used. The relative motion between the growing surfaces of the crystals 4 and the nutrient solution 6 may be increased by increasing the speed of rotation of the gyrator shaft 12, and by a more frequent rate of reversal of its direction of rotation. As an example, the gyrator shaft 12 may reverse its direction of rotation every 1, 2, 3 or more turns or revolutions and as a particular example, the gyrator shaft may reverse its direction of rotation about every 10 revolutions, with revolutions at the rate of about 30 per minute for example. The diameter of the crystallizer tank 8 will determine in large measure the rate of rotation of the gyrator 12 in general the rate decreasing as the tank 8 diameter increases.

In the reciprocating rotary type crystallizer of this invention it will be noted that the effective circulation of the nutrient solution 6 with respect to the growing surfaces of the crystals 4 is relatively very large and consequently satisfactory crystals 4 may be grown not only with the solution flowing parallel to the optic axis Z of the crystal 4 as illustrated in Fig. 4, but also flowing perpendicular to the Z axis of the crystal 4 as illustrated in Fig. 1; or in other positions such as when the crystal 4 is rotated on its own Z axis, as illustrated in Fig. 7, with or without bodily translation movement thereof through the solution 6. The combined reciprocating rotary motion of the crystals 4 in the nutrient solution 6 results in growing the crystals 4 uniformly, rapidly and in large size. At the same time, the rotary motion of the gyrator 10 and 12 creates a vortex in the solution 6 which bunches the extraneous seeds 80 at the center of the bottom 7 of the container 3 where they are redissolved in the thin layer of unsaturated solution 6 which is locally produced at the bottom part 7 only of the container 3 by the increased temperature there produced immediately above the heaters 44, 46 and 50 and provided they are not of larger size than is commensurate with the thickness of said unsaturated layer. It is a fact, however, that large size extraneous seeds can almost always be avoided by the employment of careful operating techniques, so that the small size extraneous and spontaneous seeds which appear in spite of careful operating conditions are the more important, and it is precisely these which the present method is intended to control.

The unsaturated layer of the solution 6 is

probably confined mainly to a location immediately above the heaters 44, 46 and 50. The whole of the bottom 7 or 7A of the container 8 need not be covered with the unsaturated layer of solution but only a portion of the bottom 7 or 7A where the spurious crystals 80 are aggregated. This latter condition is preferable for the reason that only a limited amount of heat can ordinarily be applied to the container 8 from the heaters 44, 46 and 50, and the more limited the area where the heat is applied the more unsaturated the solution 6 can be made and hence the more effectively can the spurious seeds 80 be dissolved.

The heating coils 44, 46 and 50 are mounted immediately beneath the bottom 7 of the tank 8 and supply heat to the solution 6, and are so arranged that the heating effect is most intense at the center of the bottom 7 of the container 8. When the gyrator 10 and 12 is turning in either of its two opposite directions of rotation, the solution 6 is moved by the gyrator 10 and 12 and forms a vortex in the solution 6 along the vertical axis of the tank 8. Spurious seeds 80 or other seeds spontaneously formed in the solution 6 are concentrated in the center of this vortex and drop to the center of the bottom 7 of the container 8. The heat supplied at this location by the heaters 44, 46 and 50 will cause the small seeds 80 there located to dissolve while at the same time the crystals 4 mounted above the bottom 7 on the gyrator 10 will grow. This useful condition comes about by raising the temperature above the saturation temperature of the solution 6 only at the extreme bottom 7 of the container 8 by means of the heaters 44, 46 and 50, or by introducing suitably heated solution through the inlet pipe 72 shown in Fig. 2 at the apex of the cone at the bottom 7A of the container 8. A thin layer of the solution 6 at the bottom region 7 or 7A of the container 8, where heat is supplied by the heater means 44, 46 and 50, is raised in temperature above the saturation temperature of the solution 6. One of the important properties of this type of crystallizer is that it will concentrate or bunch spurious or spontaneous seeds 80 in a region where they can be promptly destroyed by being dissolved into an undersaturated portion of the nutrient solution 6.

It will be understood that one of the problems in connection with the growing of crystals 4 is the seemingly spontaneous appearance of extraneous seeds 80 in the bath 6, and the development of spurious seeds introduced as dust on the intentionally planted seeds or falling into the solution 6 from the atmosphere of the room at the time of planting. If too many of these extraneous seeds 80 are formed in the bath 6, too much material may be removed from the solution to enable crystals 4 of large dimensions to be grown and it becomes important to control these extraneous seeds 80 before or when they are formed. The extraneous seeds 80 accumulate on the bottom 7 or 7A of the tank 8 and due to the vortex in the solution 6 created by the rotary movement of the gyrator 10 and 12, and also by the crystals 4 being grown, the extraneous seeds 80 accumulate at the center of the bottom 7 of the tank 8. It is here that extra heat may be supplied to the solution 6 which due to the increased temperature is less saturated at this point than in the upper regions of the solutions 6 disposed about the planted growing crystals 4. This extra heat supplied at the bottom 7 of the solution 6

is sufficient to curtail the undesired growth of the extraneous seeds 80 relative to the desired growth of the planted seeds 2. The vortex caused in the nutrient solution 6 by the rotation of the gyrator 10 and 12 may be utilized to pick up the extraneous seeds 80 and deposit them in the center of the bottom 7 of the tank 8. The temperature gradient of the solution 6 there is unsaturated and the extraneous seeds 80 are actually dissolved there while at the same time the planted crystals 4 on the rotating member 10 are growing. A favorable placement of the heaters 44 and 46 in combination with the vortex action of the rotating liquid 6 will, due to the centrifugal action, give a density and temperature gradient outwardly from the axis of the cylindrical tank 8 to the cooler outer ambient temperature. This combination of factors makes it possible to dissolve the extraneous seeds 80 which are formed in the nutrient solution 6 without interrupting the growth of the planted crystals 2 to be grown.

The reciprocating rotary gyrator 10 and 12 as mounted in the container 8 may take various forms, one of which is illustrated in Figs. 1 and 1A. The container 8 may be a cylindrical tank of "Pyrex" glass or metal, and the seeds 2 to be grown are mounted through or in rectangular openings or holes arranged in a circle on a circular disc 10 which may be a stainless steel disk, and are so set in the holes in the disk 10 that the optic axis Z, which is the axis extending from apex to apex, of the crystals 4 is perpendicular to the flat surface of the circular disk 10. The seeds 2 may also be mounted, as shown in Fig. 1A, so that the diagonal of the rectangular a axis cross-section which is perpendicular to the optic axis Z lies either along or at right angles to the adjacent diameter of the rotatable steel disk 10. The disk 10 carried by the reciprocating rotatable shaft 12 is caused to change its direction of rotation periodically, making 2 or more turns in one direction of rotation and then the same number of turns in the opposite direction of rotation. As illustrated in Fig. 1A, the crystal 4 may be placed with its a axis rectangular cross-section diagonal always in the direction of travel, and the periodic change in the direction of rotation results in a motion for the crystal 4 such that over a period of time all like or similar crystal faces experienced substantially the same relative motion between the crystal faces and the nutrient solution 6. This makes for uniform growth of the crystals 4 on all like growing surfaces and permits a relatively rapid crystal growth without defects. The crystals 4 grow nearly uniformly on both the top side and underside of the supporting disk 10 so that full crystals 4 are obtained.

Fig. 2 is a view in section illustrating a tank arrangement which may be of the type illustrated in Fig. 1, but provided with a bottom 7A which is made of cone-shape in order to more readily bunch the extraneous seeds 80 at the center of the bottom 7A of the container 8 where the spurious seeds 80 may be redissolved into the nutrient solution 6 by means of the heater resistances 44 and 46 disposed adjacent the center of the bottom 7A of the container 8 and also to give a convenient method of introducing the solution 6 into the crystallizing tank 8 where an isothermal method of crystal growing is to be employed.

Fig. 3 is a perspective view of an alternative form of gyrator mount which may be utilized to

accommodate a very large number of small crystal seeds 2. The seeds 2 may be drilled and individually mounted on the extreme ends of each pair of $\frac{1}{8}$ -inch diameter stainless steel wires 10A which may extend horizontally through holes in and be carried by the rotatable rod or shaft 12 at suitable spaced intervals along the length of the vertical rod 12. This type of support may be conveniently used for example in growing and fattening operations on small size crystal seed materials 2, when used as a reciprocating rotary type gyrator in an arrangement of the type illustrated in Figs. 1 and 2. It will be understood that any convenient number of horizontal support wires 10A may be spaced at intervals along, and around the surface of, the vertical gyrator shaft 12. The stainless steel wires 10A may be anchored in horizontal pairs in the supporting shaft 12 which may be a rod made of methacrylate resin or metal operated as a reciprocating rotary gyrator shaft.

Fig. 4 is a perspective view of another modification for the gyrator shaft 12 and the crystal support wires 10A, and illustrates an arrangement wherein the crystal seeds 2 may be drilled with one or more holes at an edge face and mounted on the support wires 10A. The wires 10A may be made of $\frac{1}{8}$ -inch diameter stainless steel rods and inserted in suitable small and shallow holes 1 drilled in the crystal seeds 2. It is convenient, though not necessary, to use a short length of plastic sleeve or tubing 3 covering the part of the stainless steel rods 10A where the crystal seed 2 is mounted. The plastic sleeve 3 permits easy removal of the crystal 2 from the mounting rods 10A without chipping the crystals, and also provides a friction fit for the crystal 2 with respect to the mounting rods 10A so that it is not easily dislodged from the mounting rods during the growing of the crystal 2. In Fig. 4, the crystal seed 2 and the crystal bar 4 grown therefrom are shown as being positioned with the optic axis Z thereof disposed in the direction of travel, instead of perpendicular thereto as illustrated in Fig. 1. Also, in Fig. 4, a pair of crystal support wires 10A is shown as being positioned in the vertical plane, instead of in a horizontal plane as illustrated in Fig. 3. It will be understood that these are alternative arrangements.

Fig. 5 is a perspective view of another form of reciprocating rotary gyrator mount which may be conveniently used to grow larger crystals 4 such as, for example, those having an a axis cross-section perpendicular to the optic axis Z of the order of two inches square or more. In this arrangement, supporting blocks and bars 10B of methacrylate resin or other suitable material may be secured by suitable bolts and nuts to the slotted vertical reciprocating rotary rod 12, and a pair of horizontal stainless steel wires 10A may be provided at each of the outer ends of the blocks and bars 10B and inserted in holes drilled in the seed crystals 2 in the manner illustrated in Fig. 4. It will be understood that any convenient number of crystal supporting bars 10B may be spaced at intervals along the vertical length of the gyrator shaft 12.

Fig. 6 is a perspective view of another form of reciprocating rotary gyrator mount which may be used to grow crystals 4 having a large a axis cross-section perpendicular to the optic axis Z. In this arrangement, the reciprocating rotary shaft 12 may carry a series of vertically spaced horizontal rods 10C which are secured to corresponding U-shaped supports 10D constructed

of methacrylate resin or other suitable material. Pairs of stainless steel horizontal wires 10E carried by the prongs of the U-shaped supports 10D are inserted in holes drilled in each seed crystal 2 to be grown to a full size crystal 4. The crystals 4 may be grown to large size. It will be understood that any convenient number of horizontal rods 10C may lie at spaced intervals along the vertical length of the gyrator shaft 12.

Fig. 7 is a view of another form of reciprocating rotary type mount which may be used for growing a single large crystal 4 such as, for example, a crystal bar 4 having an *a* axis cross-section, which is perpendicular to the optic axis Z, of the order of up to four inches or considerably more. In this arrangement, the crystal bar 4 is turned or rotated by the reciprocating rotary shaft 12 about a central line which extends along the central optic axis Z of the crystal bar 4. The initial seed crystal 2, which is shown in outline in Fig. 7, may be drilled and carried by pairs of horizontal wires 10E which are supported at each of their opposite ends in openings in two "Lucite" or methacrylate resin bars 10F disposed at opposite sides of the crystal bar 4. The crystal supporting bars 10F may be carried by two upright rods 10G and a horizontal support 10H secured to the rotatable gyrator shaft 12. The axis of the shaft 12 may be coaligned with the vertical central optic axis Z of the crystal bar 4 and rotate the crystal bar 4 about that center line axis, first turning in one direction and then in the opposite direction of rotation.

While the reciprocating rotary gyrator type of crystallizer has been described hereinbefore particularly in connection with the growing of crystals of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$), it will be understood that it may be utilized for growing not only this and other crystals 4 of the same general form but also for growing crystals generally, such as Rochelle salt and other tartrate crystals, the cube-shaped crystals of sodium chlorate, the tetrahedral crystals of sodium bromate, and also many other types of crystals grown from a suitable nutrient solution 6.

Fig. 8 is a perspective view of a crystal bar 4 comprising ammonium dihydrogen phosphate grown from a seed crystal which may be any suitable seed crystal, various forms for which are illustrated in Figs. 8 to 14. The crystal bar 4 has an optic axis Z which extends along the length of the prism faces in the apex to apex direction of the crystal bar 4. By convention, the optic axis Z is also designated as the *c* axis. Perpendicular to the optic axis Z are the two mutually perpendicular *a* axes, sometimes called the X and Y axes, which in the example illustrated extend along the base lines of the cap or pyramidal faces of the crystal bar 4.

The crystal bar 4 may be grown to various sizes and shapes, such as, for example, a long crystal bar 4 of *a* axis dimensions up to four inches or more square in cross-section, and fifteen inches or more in length along the optic axis Z; or in the smaller sizes two inches more or less in cross-section in the *a* axis dimensions, and ten inches or less in length along the optic axis Z. The size of the crystal bar 4 depends upon the time of growing and other factors. In the case of ammonium dihydrogen phosphate, a crystal bar 4 of two inches in the *a* axis dimensions may be grown in a matter of some four weeks time from an initial length of three inches to a final length of six

inches, and much larger crystals 4 may be grown in a longer time. The shape of the crystal bar 4 depends upon the character of the nutrient solution 6 from which the crystal bar 4 is grown, and the seed 2 from which the crystal bar 4 is grown. The seed crystals 2 and also other crystals intended for use as piezoelectric elements, may be cut from the mother crystal bar 4.

As shown in Fig. 8, the crystal plate 2a is a Z-cut plate, which may be cut from the central region of the mother crystal bar 4, and which may be used as a seed crystal 2. The crystal plate 2b is also a Z-cut plate which may be cut from the crystal bar 4 at regions other than from the central region of the crystal bar 4. A Z-cut plate is one which has its major faces disposed perpendicular to the Z or optic axis. The Z-cut plate 2b may be used as a seed crystal 2, or, as a finished end piezoelectric product. The crystal plate 2c is a 45-degree Z-cut plate which may also be used as a finished end piezoelectric product. A 45-degree Z-cut crystal plate 2c is one which has its major faces perpendicular to the optic axis Z and its length and width dimensions inclined at an angle of 45 degrees with respect to the *a* axes, as illustrated in Fig. 8 at 2c. Other examples of crystal seeds 2 which may be cut from the crystal bar 4 are the cap seed with Z-cut base 2d, and the wedge seed with Z-cut base 2e. The two wedge faces of the wedge type seed 2e are cut parallel to the cap or pyramidal faces of the crystal bar 4.

It will be understood that any piece of single crystal cut from the crystal bar 4 of Fig. 8 is a possible seed 2 from which a crystal bar 4 may be grown. In commercial crystal bar growing, however, it is often desirable that the crystal bar 4 grow with predetermined approximate dimensions and this requirement involves the dimensions of the seed 2. For example, where the end use of the crystal bar 4 is the production of 45-degree Z-cut piezoelectric plates 2c cut therefrom, and if one such 45-degree Z-cut plate 2c is expected from each Z-cut plate 2b, the two mutually perpendicular *a* dimensions of that Z-cut plate 2b and of the crystal bar 4 should be of slightly greater magnitude than the sum of the two adjacent sides of the required 45-degree Z-cut plate 2c divided by the square root of two. Any piece of single crystal oriented with its crystallographic axes Z and *a* coinciding with those of the crystal bar 4 to be grown, will be a suitable seed for that crystal bar 4 provided the seed touches each of the expected four prism faces of the crystal bar 4 in at least one point and does not extend beyond these four expected prism faces. In general, the kinds of seeds 2 employed for growing a crystal bar 4 may be classified broadly as (a) seeds which are bounded by grown surfaces only, (b) seeds with some or all cut surfaces approximately parallel to the natural faces, the uncut surfaces being natural crystal surfaces, and (c) seeds with some or all surfaces which are neither natural crystal surfaces nor cut approximately parallel to natural faces. Some of the various types of crystal pieces which may be used as seeds are illustrated in Figs. 8 and 9. These include the Z-cut plate 2a, a capped seed (Fig. 9) which may be grown from the Z-cut plate 2a of Fig. 8, a double wedge seed 2e, a cap seed with wedge 2d and 2e, and a cap seed with Z-cut base 2d which is taken from an end section of the crystal bar 4 and, accordingly, is usually free from imperfections and may be used as a seed without further preparation.

Fig. 9 is a perspective view illustrating a capped type seed crystal 2f which may be grown into a crystal bar 4. The capped seed crystal 2f which is bounded only by grown surfaces, may be grown and prepared from a Z-cut plate 2a of Fig. 8 in a separate growing operation with the nutrient solution 6 circulating in directions normal to the Z axis until the natural caps and pyramid faces are well formed. The more desirable capped seeds 2f are generally those with the shortest Z-axis dimension. Large size capped plate seeds 2f up to 6 inches square in a axis cross-section perpendicular to the Z axis and larger may be easily grown using a type of mount as illustrated in Figs. 1 to 7. While better results may generally be obtained more consistently with Z-cut plate seeds 2b which are free from flaws and inclusions of misoriented crystalline material, the capping of the crystal seed 2f may be carried out successfully with obviously imperfect Z-cut plates 2a. It is unimportant in growing capped seeds 2f if the central portions of the initial seed plate 2a are imperfect, disordered or have a hole therein, since a suitable capped seed 2f will be produced if the edges of the initial Z-cut plate 2a are of clear material of uniform orientation and at least $\frac{1}{16}$ -inch thick in the Z-axis direction, the pyramids of the capped seed 2f covering all faults in the center of the initial plate 2a. Also, seed plates 2a with broken or cut corners and chips out of the edge will heal satisfactorily when grown into a capped seed 2f. If the initial seed plate 2a has only a small quantity of misoriented material interior to the edges of the initial seed plate 2a, the pyramidal caps may form as easily as though the initial plate 2a were perfect and contained no such misoriented nuclei. A perfect capped seed 2f will result from a plate 2a the prism faces of which contain no misoriented crystalline material. Purely geometrical flaws in the seed plate 2a such as missing corners or edges result in little difficulty in obtaining good capped seeds 2f, provided the exposed crystal in the seed plate 2a is of a single uniform orientation.

It has been known in the art that the addition of small amounts, of the order of 0.001 mol per liter, of iron or of aluminum to the nutrient solution 6 used for growing the capped plates 2f of Fig. 9 increases the stability of the supersaturated solution 6 in a way to inhibit the formation of spurious or spontaneous seeds in the nutrient solution 6 and controls the prism face growth especially on seed plates 2a with misoriented nuclei, and also aids in causing the plate 2a to cap more quickly by causing tapering. Good results however may be obtained with or without such iron or aluminum solution additives. Capping operations on seed plates 2a take only a few days and the question of spurious seeds is, therefore, of relatively little moment in seed crystal capping. The usefulness of such iron or aluminum additives occurs when poor quality seed plates 2a are used, since the control of the prism face growth does not permit the misoriented nuclei to develop in the capping of the Z-cut plates 2a.

Good and consistent capping of such Z-cut plates 2a of Fig. 9 may be attained from a saturated nutrient solution 6 of primary ammonium dihydrogen phosphate with an additive to the capping solution 6 of sulphate, which may be about 4 grams of sulphate per liter of the solution 6 used for growing the capped seed 2f. A solution 6 prepared with this added sulphate has a beneficial influence on the pyramidal capping 2f of the seed plate 2a. The capping solution 6 may

contain the added sulphate referred to, as well as a small amount of iron or of aluminum which may be of the order of 0.001 mol per liter. It will be understood that the nutrient solution 6 of ammonium dihydrogen phosphate used for growing a capped seed crystal 2f of Fig. 9 may contain such a sulphate additive in order to improve the capping of the capped seed crystal 2f which may be thereafter used for growing a long crystal bar 4 therefrom. The improved capping of the capped seed crystal 2f consists in such improvements as the formation of a complete pyramidal cap 2f with unbroken surface in a shorter growing time and involving a shorter Z-axis growing distance, and a substantial reduction of the tendency for the capped seeds 2f, especially large ones that are 2 inches or more in a-axis dimension, to crack spontaneously during their formation. The sulphate additive may be added to the nutrient solution 6 in the form of ammonium sulphate or any other suitable water soluble sulphate which does not introduce other ions whose effects are undesirable.

Figs. 10 to 14 are side views illustrating several ammonium dihydrogen phosphate crystal bars 4 grown from seeds 2 of various types. The division of the bar 4 into sections generally showing the seed 2, the caps b1 and b2, flaws f, and the usable crystal sections g of the crystal bar 4 are illustrated. The Z-cut seed plate 2a, which is illustrated in Fig. 10, has a tendency to give flawed cones 3 on each of the two major faces of the Z-cut seed plate 2a and accordingly is somewhat less economical of crystal material when used in growing a crystal bar 4 therefrom. The cap seed with Z-cut base 2d, which is illustrated in Fig. 11, has a tendency to give a flawed cone 3 on the Z-cut base side only, but is quite economical of crystal material when used for growing a crystal bar 4, and moreover it costs little, ordinarily being scrap from the normal crystal bar 4 cutting operation. The capped Z-cut plate seed 2f, the cap seed with wedge 2d plus 2e and the double wedge seed, all of which are illustrated by the diagram in Fig. 12, are a little less economical of material than the cap seed with Z-cut base 2d, which is illustrated in Fig. 11. The cap seed with diagonal base, which is illustrated in Fig. 14, is also somewhat uneconomical of crystalline material when used in growing a crystal bar 4.

The diagonal type seed plate 2g, which is illustrated in Fig. 13, is cut so that the two major surfaces thereof are parallel to, and approximate closely the orientation of a 101 plane, or in other words a pyramidal cap face, of the ammonium dihydrogen phosphate crystal 4. A crystal bar 4 may be grown from such a diagonal seed plate 2g that shows such perfect joining of the crystal bar onto the diagonal type seed 2g that the whole crystal bar 4 can thereafter be used for cutting therefrom unflawed usable Z-cut piezoelectric plates 2a. The major surfaces of the diagonal seed plate 2g may depart from the true 101 plane, which is the true cap face orientation of the crystal bar 4, by as much as about one-half degree of angle and still give a diagonal seed plate 2g capable of yielding a substantially perfect joint and, hence, give a crystal bar 4 all of which can be economically used without waste for making piezoelectric plates therefrom. This gives the diagonal seed plate 2g a considerable advantage over other types of seeds 2 used for growing a crystal bar, especially where 45-degree Z-cut piezoelectric plates 2c are to be manufactured in the larger sizes. Crystal bars 4 grown from di-

agonal seed plates 2g are free from phantom veils or flaws 3 running through the interior of the bar 4. The diagonal seed plate 2g is disclosed and claimed in a copending application, Serial No. 598,693 filed June 11, 1945, by C. J. Christensen, now United States Patent No. 2,442,755 dated June 8, 1948, assigned to Bell Telephone Laboratories, Incorporated.

It will be understood, however, that it is possible to grow a perfect crystal bar 4 from any suitable seed 2, several types of which are illustrated in Figs. 3 to 14. In general, seeds with natural grown surfaces only or seeds with surfaces cut parallel to naturally grown surfaces give good crystal bars 4. Also, in general, seeds 2 of any type may have flawed material therein provided this flawed material is confined to the center portions only thereof. Thus, the diagonal seed plate 2g, which may be cut from the center region of the crystal bar 4 in Fig. 9 grown from a capped Z-cut plate 2f, may have flawed material on its two major surfaces; but since these flawed surfaces are surrounded by a perimeter of good solid crystal, such a diagonal seed plate 2g will heal over quickly when grown and give a good crystal bar 4. Also, the Z-cut plate seed 2a is a satisfactory seed for growing a crystal bar 4 when grown in the reciprocating radial type crystallizer of this invention, wherein the crystal bar 4 can be successfully grown with the nutrient solution 6 circulating in either perpendicular or longitudinal relation with respect to the Z axis, as shown in Figs. 1, 4, 5, 6 and 7, for example.

Although this invention has been described and illustrated in relation to specific arrangements, it is to be understood that it is capable of application in other organizations and is, therefore, not to be limited to the particular embodiments disclosed.

What is claimed is:

1. The method of growing pyramidal capping upon the major faces of a Z-cut type ammonium dihydrogen phosphate crystal plate which consists in forming the pyramidal capping while depositing solute onto the crystal plate from a nutrient solution of ammonium dihydrogen phosphate in the presence of water-soluble sulphate present in the solution in sufficient amount to cause effective pyramidal capping of the crystal plate.

2. The method of growing a plurality of individually mounted crystals simultaneously in a single contained body of nutrient solution while simultaneously destroying loose crystals therein, which consists in revolving the several mounted crystals together simultaneously in bodily translation movement through the upper part of the single body of solution in their respective circular paths around a common substantially vertical central axis of rotation radially spaced inwardly entirely away from the mounted crystals, periodically revolving the several mounted crystals alternately in each of the two opposite directions of rotation around the common vertical axis of rotation, at a speed sufficient to produce simultaneously a central vertical vortex in the solution, for a substantially equal number of more than one revolution in each of the opposite directions of rotation and periodically reversing 180 degrees the directions of effective flow of the saturated upper part of the solution with respect to the several mounted growing crystals, while thereby simultaneously gathering together loose undesired crystals in the region of the lowest part of the body of solution adjacent the vortex region

therein, applying sufficient heat to the lowest part only of the single body of solution to render the solution substantially unsaturated in the lowest part only thereof where the loose undesired crystals to be destroyed are gathered together by the vortex and simultaneously to render the solution substantially supersaturated in the upper part thereof where the mounted growing crystals are revolving, and adding solute to the solution sufficient in amount to replenish the solute deposited from the solution onto the mounted growing crystals.

3. The method of growing a plurality of individually mounted crystals simultaneously in a single contained body of nutrient solution while simultaneously destroying loose crystals therein which consists in revolving the several mounted crystals together simultaneously in bodily translation movement through the upper part of the single body of the solution in their respective circular paths around a common substantially vertical central axis of rotation radially spaced inwardly entirely away from the mounted crystals, periodically revolving the several mounted crystals alternately in each of the two opposite directions of rotation around the common vertical axis of rotation, at a speed sufficient to produce simultaneously a central vertical vortex in the solution, for a substantially equal number of more than one revolution in each of the opposite directions of rotation and periodically reversing 180 degrees the directions of effective flow of the saturated upper part of the solution with respect to the several mounted growing crystals, while thereby simultaneously gathering together loose undesired crystals in the region of the lowest part of the body of solution adjacent the vortex region therein, applying heat to the lowest part only of the single body of solution at a temperature suitable to render the solution continuously unsaturated in the lowest part only thereof to destroy loose undesired crystals there gathered together by the vortex and simultaneously to maintain the upper part of the solution at a temperature suitable to render it continuously sufficiently supersaturated to grow the mounted crystals revolving therein.

4. A crystallizer comprising a single stationary container having a single chamber, the upper part of said chamber comprising a stationary crystallizing chamber and the lowest part only of said chamber adjacent the bottom only of said container comprising a decrystallizing chamber, heat insulating means covering at least a part of said container, a rotatably mounted gyration positioned in said crystallizing chamber, said gyration comprising a shaft having a substantially vertical axis, radial type means carried by said shaft and extending outwardly therefrom in a plurality of different radial directions around and on opposite sides of said shaft, and a plurality of crystal work mounting means carried by said radial type means at spaced points thereon positioned adjacent the extreme outermost ends thereof towards the sides of said container and spaced entirely away from and out of alignment with respect to said axis of said shaft, means connected with said shaft for periodically rotating said gyration relative to said container alternately in opposite directions of rotation for a substantially equal number of at least two revolutions in each of said opposite directions of rotation, a heater comprising an electrically heated resistor disposed adjacent said bottom only of said container below said gyration, and a

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temperature responsive device disposed in said container and electrically connected with said heater and made responsive to a predetermined temperature value corresponding to predetermined different temperature values respectively required in said decrystallizing or lowest part only of said chamber and in said crystallizing or upper part of said chamber in the region of said gyrator.

5. A crystallizer comprising a single stationary container having a single chamber, the upper part of said chamber comprising a stationary crystallizing chamber and the lowest part only of said chamber adjacent the bottom only of said container comprising a decrystallizing chamber, heat insulating means covering at least a part of the sides of said container, a rotatably mounted gyrator disposed in said upper or crystallizing chamber part of said container and having a substantially vertical axis of rotation disposed substantially centrally with respect to said sides of said container, said gyrator comprising a substantially vertical shaft having an upper part extending through an opening in the top of said container and a lower part disposed in said upper chamber part of said container, radial type supports carried by said lower part of said shaft and extending outwardly therefrom in a plurality of different radial directions around and on opposite sides of said shaft, and a plurality of crystal work mounting means carried by said radial type supports at spaced points thereon positioned adjacent the extreme outermost ends thereof towards said sides of said container and spaced entirely away from and out of alignment with respect to said axis of rotation of said shaft, said work mounting means comprising wires having crystal work supporting ends, means connected with said shaft for periodically rotating said gyrator relative to said container alternately in opposite directions of rotation for a substantially equal number of at least two revolutions in each of said opposite directions of rotation, a heater comprising an electrically heated resistor disposed adjacent said bottom only of said container below said gyrator, and a temperature responsive device disposed in said container and electrically connected with said heater and made responsive to a predetermined temperature value corresponding to predetermined different temperature values respectively required in said decrystallizing or lowest part only of said chamber and in said crystallizing or upper part of said chamber in the region of said gyrator.

6. A crystallizer comprising a single stationary cylindrical-shaped enclosing container having a single chamber, the upper part of said chamber comprising a stationary crystallizing chamber and the lowest part only of said chamber adjacent the bottom only of said container comprising a decrystallizing chamber, heat insulating means covering at least a part of the sides, top and bottom of said container, a pivotally mount-

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ed gyrator disposed in said crystallizing chamber and having a substantially vertical axis of rotation disposed substantially centrally with respect to said sides of said container, said gyrator comprising a substantially vertical shaft having an upper part extending through an opening in said top of said container and having a lower part disposed in said crystallizing chamber, radial type supports carried by said lower part of said shaft at spaced positions along the axial length thereof and extending outwardly therefrom in a plurality of substantially horizontal different radial directions around and on opposite sides of said axis of said shaft, and a plurality of crystal work mounting means carried by said radial type supports at spaced points thereon positioned at the extreme outermost ends thereof adjacent said sides of said container and spaced entirely away from and out of alignment with respect to said axis of said shaft, said work mounting means comprising wires having crystal work supporting ends and plastic type sleeves covering said work supporting ends of said wires, means connected with said shaft for periodically rotating said gyrator relative to said stationary container alternately in opposite directions of rotation for a substantially equal number of more than two revolutions in each of said opposite directions of rotation, a heater comprising an electrically heated resistor disposed adjacent said bottom only of said container below said gyrator, and means including a temperature responsive device disposed in said crystallizing chamber and electrically connected with said heater for regulating the amount of heat supplied by said heater at said bottom of said container in accordance with predetermined different temperatures required for said upper crystallizing and lower decrystallizing chambers respectively, said temperature responsive device being made responsive to a predetermined temperature value corresponding to the values of said predetermined different temperatures.

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