April 5, 1966 R. C. LINARES ET AL 3,244,488

PLURAL DIRECTIONAL GROWING OF CRYSTALS

Filed June 6, 1963

Fig. 1.

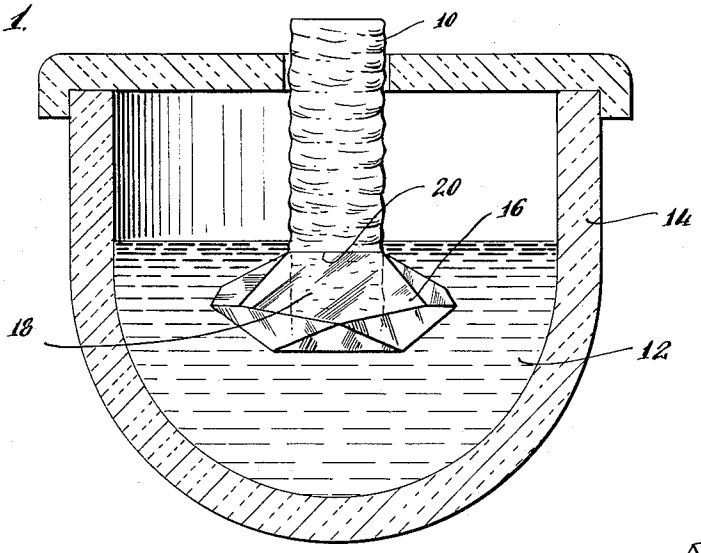
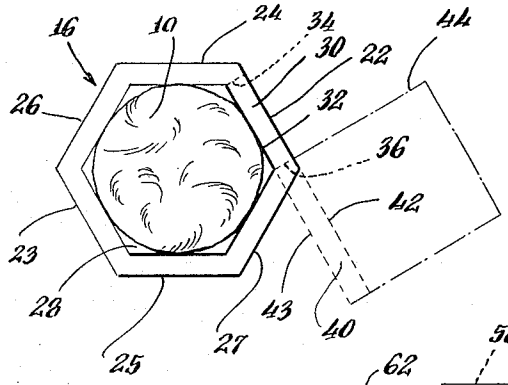


Fig. 2.



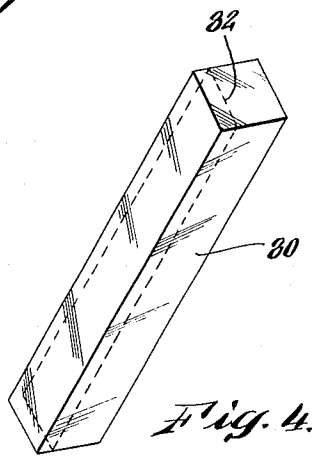


Fig. 4.

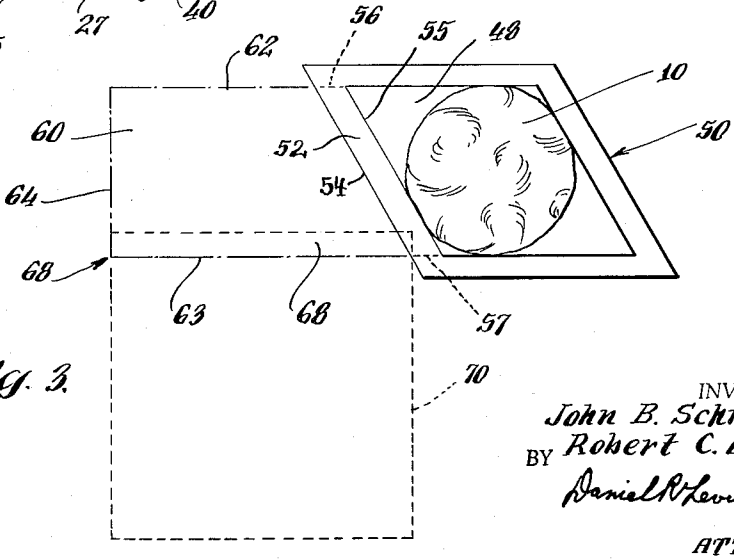


Fig. 3.

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PLURAL DIRECTIONAL GROWING OF CRYSTALS

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This invention relates to the growing of crystals in a flux. More particularly, the invention concerns a method for producing crystals which are relatively free of defects in their crystal structure so as to be highly suited for specialized uses.

Among the various current methods of growing crystals are the flame fusion or Verneuil method and the various methods in which the crystal is precipitated from a saturated solution of the crystal material in a flux of molten inorganic material. The flame fusion technique, as its name implies, utilizes a flame as a local heating source for melting the crystal material as it is slowly fed thereto as a fine powder. The powder melts as it enters the hot region of the flame, forming molten droplets which are then allowed to cool at a particular location (for example, directly below the flame) so as to gradually build up the crystal at this location. Another presently utilized technique, flux growing, involves the dissolving of crystal material in an inorganic flux (which is composed of metallic salts or oxides including mixtures thereof) so as to form a saturated solution at an elevated temperature. By slowly cooling the solution, the supersaturated crystal material is caused to precipitate out. This procedure may be done in either the absence or the presence of seed crystals of the material to be precipitated The former may be termed growth by slow cooling and the latter may be termed flux growth in the presence of a seed. In a variation of this latter method, the saturated solution may be in contact with excess crystal material solute, which contact may be in a somewhat hotter part of the flux so as to maintain the solution supersaturated with respect to the cooler part in which the crystal is grown. This excess slowly dissolves providing a continuous source of material to replace that which has been deposited on the seed crystal.

The flame fusion and flux methods have various advantages and disadvantages relative to each other. In particular, the flame fusion technique presently allows the production of larger crystals and is therefore the predominant commercial process. On the other hand, crystals grown by this method exhibit an extremely large number of structural defects, such as various types of dislocations as well as substantial axis wander. Crystals grown from a flux have been limited as to size, but contain fewer flaws, which are also generally less extensive. Therefore, prior to the hereinafter disclosed invention, one could obtain either large highly imperfect crystals or small substantially perfect ones, depending upon the type of growth utilized. With the advent and development of solid masers and, in particular, solid optical masers (or lasers), the need for larger, relatively flaw-free crystals (such as rubies) has become more and more acute. It has now been determined that flaws appreciably decrease the efficiency of a given size crystal laser and prevent laser systems from achieving their theoretically predicted performance level. For this reason, it is particularly important to utilize crystals which are as free of flaws as is possible for such uses. The invention provides a method of growing relatively large crystals by a flux growth method, thereby obtaining large crystals more closely approaching perfection than has been previously possible. This may be accomplished in a relatively short total growth time as will appear hereinafter.

The invention is based on the observation that a relatively imperfect (flame fusion growth) crystal may be utilized as a seed in a flux growth method without causing at least some of the flaws of the original seed to be propagated in all of the newly formed crystal extension. It has been determined that the flaws will propagate into the newly grown crystal only into those parts which are direct extensions of the seed crystal but will not, in general, be propagated into those parts of the newly grown crystal which do not form a direct extension of the seed crystal. The latter portions may then be utilized as seeds to grow (by additional flux growth operations) a relatively flaw free crystal. By intentionally causing at least one growth to be in a direction along a crystal axis different from the first growth, the part of the crystal grown will be free of most flaws of the original seed. The newly grown portions of the crystal may be utilized to grow a laser crystal along a third axis different from the second axis (but the third axis may be the same as the first). In this manner, the growth steps tend to eliminate reoccurrence of the original seed crystal flaws, so that the final material is relatively flawless. Since the inventive method may be utilized to grow many different types of crystals, the actual number of growth steps used may be more or even less than outlined above.

An object of the invention is the production of large, relatively flawless crystals in a relatively short time.

Another object of the invention is the production of crystals which contain much fewer flaws than the seed from which they originated.

A further object of the invention is the production of relatively flawless crystals by means of flux growth utilizing as the original seed a relatively imperfect crystal obtained from a different growing technique.

Further objects and advantages of the invention will be obvious to one skilled in the art upon reading the foregoing and following description in conjunction with the accompanying drawing in which:

FIGURE 1 is an elevation of flux growth of a crystal illustrating how flaws in a flame fusion grown seed tend to propagate into the flux grown crystal;

FIGURE 2 is a schematic plan view of a hexagonal section crystal illustrating how a part thereof may be utilized to grow a relatively flawless crystal;

FIGURE 3 is a schematic plan view corresponding to FIGURE 2 of a different shape crystal, illustrating how it may be utilized to form a relatively perfect final crystal; and

FIGURE 4 is a perspective view of a typical final crystal, grown according to either FIGURE 2 or FIGURE 3.

In FIGURE 1 a rod-like crystal **10**, previously grown by, for example, the flame fushion method, is illustrated as slightly immersed in a saturated flux **12** contained in furnace **14**. It is assumed that the flux has been already cooled from a high temperature at which it was saturated with the same material as that of the seed crystal. For this reason a substantial amount of the saturated solute has precipitated on the lower end of seed crystal **10** so as to form the flux grown crystal **16**. As diagrammatically illustrated by the shading **18** in the central part of the grown crystal **16**, the flaws present in the lower face **20** of the seed crystal **10** tend to propagate to those areas (at **18**) of the flux grown crystal which are built up from growth on that face. On the other hand, the edge area of crystal **16**, which have grown along different axes are relatively flaw free.

The seed crystal **10** has flaws which tend to propagate into those parts of crystal **16** which are formed by direct extension of the seed by growth thereon. The central area of the flux grown crystal **16** which is formed along the vertical axis of the seed will therefore contain those flaws (vertical shade lines) which propagate along this

vertical growth axis. The edge portions of crystal **16**, which have grown by deposition on this central portion **18** along generally horizontal axes, tend to propagate only those flaws in the central section **18** which propagate along axes other than the vertical. For this reason, such edge sections of the crystal are relatively flawless. In other words, these parts of crystal **16** which grow (in generally horizontal directions (on to the central part of the flux grown crystal do not regenerate the flaws in seed crystal **10** (represented by the shade lines in the seed).

FIGURE 2 illustrates a generally hexagonal crystal (similar to the one shown in FIGURE 1), and how the method of the invention may be utilized to produce essentially flawless crystals therefrom. This figure shows in plan view, the seed crystal **10** (which in this case extends well below the flux surface) about which the generally hexagonal crystal **16'** has been formed. Since the seed crystal **10** was produced by means of the flame fusion method, it is assumed to be generally cylindrical in shape so as to have a circle cross-section as shown in FIGURE 2. As the temperature of the flux is reduced, the dissolved crystal material will propagate about the lower end thereof. More particularly, the crystal growth will occur along each of the several crystal axes. Among these for this particular crystal are the three generally horizontal growth axes, which are perpendicular to the crystal face pairs **22, 23**; **24, 25**; and **26, 27**. The initial growth along these axes will cause the generally rounded seed crystal to be built up by highly imperfect crystal deposits in the region labeled **28**. This original growing or "capping" of the seed crystal causes subsequent growth to be along the three natural horizontal axes. If the seed crystal is originally positioned in the flux so that only its extreme lower end is actually therein, the condition shown in FIGURE 1 will soon result in which substantially all of the growth along the horizontal crystallographic axes is upon flux grown base material. On the other hand, the seed **10** shown in FIGURE 2 extends well below the surface of the flux **12** (FIGURE 1), so as to increase the growth surface (and therefore the rate). Thus, the depth of all the crystal parts shown in FIGURE 2 may be many times the cross-sectional diameter of crystal **16'** shown in FIGURE 2.

As previously explained, the parts of the crystal (such as **30**) which are formed directly on this extension **28** of the seed by growth in generally horizontal directions will contain those flaws which propagate along such horizontal growth axes (but not the flaws which propagate only in a different direction). For purposes of illustration, it is assumed that a section (shown at **30**) which has grown along the axes extending generally to the right and upward in FIGURE 2 has been chosen for the subsequent growing steps. By cutting therefrom a slab bounded by surfaces **22, 32, 34** and **36** from the crystal, a new seed crystal, relatively free of flaws of the type which propagate along the axis perpendicular to surfaces **34** and **36** is obtained. This seed crystal is then utilized to grow a crystal slab **40** (shown in dotted lines) which is propagated from face **36** in the axial direction perpendicular to surface **36**. This second growth will eliminate those flaws which exist in crystal slab **30** which only propagate along the natural crystal axes perpendicular to faces **22** (and **23**), **24** (and **25**), and **26** (and **27**). The final third growth may then be made along face **42** (or **43**) of crystal slab **40** in the direction parallel to the natural crystal axis perpendicular to surface **22** (and **23**). This last growth step will cause the final crystal **44** to be substantially free of those flaws which tended to propagate into the original crystal slab **30**. Slab **40** may be subsequently cut from final crystal **44** and utilized over and over again to grow additional final crystals.

The particular direction of growth chosen will, of course, vary depending upon the crystal grown. For this reason, FIGURE 2 is intended to be merely illustrative of one sequence of growth directions, which may be utilized to produce a relatively flawless crystal **44**. In order to more clearly point out the fact that FIGURE 2 is merely exemplary, another example is illustrated in FIGURE 3. In this figure, a flawed seed crystal **10** is introduced into a flux saturated with the crystal material as before at a high temperature. As the furnace is allowed to cool, the first growth of crystal material will cause the forming of the natural crystal habit for the particular growth conditions. This is the formation of the "capping" region **48** which immediately surrounds the seed crystal. The crystal will then grow so as to cause an ever enlarging rhomboidal configuration to be formed by the subsequent precipitated crystal material as shown at **50**. One section or slab **52** (bounded by faces **54, 55, 56** and **57**) may then be used to grow a second crystal **60** by repetition of the growth step in another saturated flux which favors growth on face **54**. This crystal **60** (bounded by the chain line sides **62, 63** and **64** and face **54**) may then be cut as shown by dash line **66** to produce a slab-shaped new seed crystal **68**. This seed crystal **68** may then be utilized to grow on one of its long faces (such as face **63**) the final relatively flawless crystal **70**. The rest of intermediary crystal **60** may be utilized to produce additional seed crystals (like **68**). Thus, the growth process illustrated in FIGURE 3, although somewhat similar to that in FIGURE 2 differs in two respects. In addition to the obvious difference involving the shape of the original crystal, the process differs in that it utilizes one of the original faces (**54**) of this crystal for the growth of the intermediary crystal (**60**). Because of this difference in choice of growth face, this intermediary crystal **60** is more extensive in area then the corresponding intermediary **40** in FIGURE 2, so that the former may be preferably sectioned to provide a plurality of similar seed crystals.

In both FIGURES 2 and 3, the depth of the various crystals in the direction perpendicular to the plane of the papers may be chosen as desired (being determined primarily by the depth of the original grown crystals **16'** and **50**). The two processes illustrated are obviously merely exemplary in that any two growth directions may be utilized to grow the intermediary and final crystal. Although the two diagrams indicate growth on only one of the two similar faces of both the two grown seed crystals, in actuality, the growth will normally occur along both opposing faces. In other words, the original slab **30** (in FIGURE 2) will produce intermediary crystal on both surface **36** (as shown at **40**) and on face **34**. Each of these intermediary crystals may be utilized as seed crystals to form final crystals. Similarly, intermediary crystal **40** would normally grow a final crystal not only on its face **42** as shown at **44**, but also on its face **43**. Thus, the FIGURE 2 process would actually produce two intermediary crystals and four final crystals from the three growth steps utilized.

In view of the fact that the tendency to propagate defects will vary in different types of crystals (both as to the constituents of the crystal and the number and directions of the faces), the number of intermediary growth steps utilized and the preferred direction of growth will generally differ depending upon the type of material, the particular crystal habit or shape, and the degree of perfection required in the final crystal. Although two of the more common crystal geometries have been used as examples in FIGURES 2 and 3 to show how the crystal habit affects the choice of growth axes, nevertheless, these two examples do not fully illustrate the many different possibilities that exist. For purposes of simplifying the illustration, all growth steps in the illustrated examples had been shown in a single plane, while, in general, the directions of growth may be in different planes. For example, the intermediary seed crystal **60** (or **40**) could obviously be utilized to grow crystals on the faces (not shown) which are parallel to the plane of the paper (i.e.

the growth direction would be perpendicular to the paper), particularly when the original depth of the crystal is relatively small. Similarly, with a crystal habit of the type shown in FIGURE 1, various growth directions which are neither parallel nor exactly perpendicular to each other may be utilized.

In general, it is preferable that each growth step is done with a seed which is quite extensive in length in at least one direction (preferably, two directions) making a substantial angle (near 90°) to the growth direction, in order to maximize the volume of material grown in any given unit time. For example, as previously stated, seed crystal **10** in each of FIGURES 2 and 3, should preferably extend well into the flux so that slabs such as **30** (FIGURE 2) and **52** (FIGURE 3) are quite extensive in the direction perpendicular to the paper. Where the seed crystal in a particular growth is extensive in both depth (i.e., in the direction perpendicular to the paper in FIGURES 2 and 3) and also in width (i.e., the direction generally transverse or more or less perpendicular to the growth direction), an even greater volume of crystal is formed per unit time. Thus, the growth of final crystals **44** (FIGURE 2) and **70** (FIGURE 3) is quite efficient, since the growth time (dependent primarily on the linear extent of growth along the growth axis) is no greater than that required to grow intermediary crystals **40** (FIGURE 2) and **60** (FIGURE 3) respectively. Similarly, the growth of intermediary crystal **60** on grown seed **52** in FIGURE 3 is quite efficient (as measured by volume grown per unit time) relative to the growth of intermediary crystal **40** on grown seed **30** (FIGURE 2), since the volume of intermediary **60** is substantially greater than that of intermediary **40** while the growing time is essentially the same (all other factors being equal). The type of growth shown in FIGURE 2, nevertheless, takes no longer to produce a (single) final crystal (**44**) than that shown in FIGURE 3 (assuming similar dimensions, growth rates, and the like). Thus, the advantage in FIGURE 3 resides primarily in the size of intermediary crystal **60** (and therefore the number of intermediary seed crystal slabs, such as **68**, which can be made therefrom), which is important only if a large plurality of final crystals are desired at one time, since each of intermediary seed crystal slabs **40** or **52** may be reused over and over again. The crystal habit, growth speed in different directions, and the properties of the final crystal desired may therefore make a growth process containing a single "inefficient" growth step (e.g., see FIGURE 2) at least as attractive and practical as the theoretically wholly "efficient" process of FIGURE 3. In any event, where other factors permit, the final growth step should be made on a grown seed crystal which already contains the longest dimension (and preferably the second longest dimension as well) of the final crystal (assuming it is not a cube). In other words, the depth of all the crystals in FIGURES 2 and 3 (i.e., the dimension perpendicular to the paper) is assumed to be the longest dimension of final crystals **44** and **70**, which therefore are long rods having the square cross-section shown in the drawings.

The above considerations are best seen in the concrete example of FIGURE 4. In this figure a long final crystal **80**, having a relatively small (essentially square) cross-section is shown as having been produced from a slab-shaped seed crystal **82**. The crystal **80** in FIGURE 4 may represent either the final grown crystal **44** in FIGURE 2 or the final crystal **70** in FIGURE 3, and seed crystal **82** corresponds to either seed crystal **40** or **68**. Thus, FIGURE 4 shows explicitly that the final grown crystal is produced without any (flux) growth in the direction of its long dimension, since the two flux growths take place across its two shorter dimensions. As previously stated, the seed crystal slab **82** may be used over and over again so that additional relatively flawless final crystals (corresponding to crystal **80**) may be made therefrom by simply growing across the relatively short substantially horizontal distance in that figure (corresponding to the same direction in FIGURE 2 and the vertical direction in FIGURE 3).

Since it is impractical to indicate the different possible faces and growth directions which may be utilized for the various crystal materials which may be purified by the invention (each of which may exhibit a plurality of different habits), only a single example of crystal material is given. As indicated in an article by R. C. Linares (one of the co-inventors of the instant application) entitled "Growth of Refractory Oxide Single Crystals" in the Journal of Applied Physics, volume 33, No. 5 (May 1962) pages 1747–49, the growth habit of alumina, corundum or sapphire (Al_2O_3) crystals may be controlled by utilizing different percentage mixtures of lead fluoride (PbF_2) and lead oxide (PbO) as the flux material. More specifically, the crystals will be rhombohedral for fluxes containing 10 to 40% PbF_2 by weight, and will be in the form of thin plates when the flux is 40 to 70% PbF_2. As noted in the first paragraph of page 1749 of the above mentioned article, small additions of Cr_2O_3 do not affect the crystal habit. Therefore by utilizing different fluxes and the invention herein described, one may purify a synthetic ruby grown by the flame fusion method so as to produce substantially perfect ruby crystals.

This growth would be accomplished as set forth previously in the specification by growing a first crystal from the flawed seed in a manner similar to that shown in either FIGURE 2 or 3. Material grown in the first flux growth (such as shown at **30** in FIGURE 2, or **52** in FIGURE 3) would then be utilized to perform a second flux growth (such as at **40** in FIGURE 2 or **60** in FIGURE 3). Finally, a third growth (corresponding to crystals **44** and **70** in FIGURES 2 and 3 respectively) will be effected. Since the relative rate of growth along different axes varies according to the constituents in the flux (as taught in the aforementioned article), most of the growth will occur in desired controlled directions. For example, if FIGURE 3 represents the process of growing a relatively flawless ruby, the growth of the crystal **60** on seed crystal **52** would be accomplished in a melt comprising a given percentage of lead fluoride (for example, between 10 and 40% by weight) so that at least most of the material would grow in the manner represented by crystal **60** (i.e., along a given direction relative to surface **54** of crystal **52**). The next growth step (utilizing part **68** of the seed and growing crystal **70**) would then be done in a substantially different flux (i.e., between 40 and 70% lead fluoride by weight), so that most of the growth would occur in a direction more or less perpendicular to surface **63** of seed **68**.

As previously stated in the specification, each of these growth steps will tend to eliminate those flaws in the original crystal seed (which was grown by the flame fusion process, for example) which do not propagate along the particular growth axis used in that growing step. Therefore the final crystal **70**, grown by a process utilizing growing steps along different axes, will be free of substantially all of the flaws originally present in the flame fusion crystal **10**. In this manner a relatively flawless ruby crystal (or other crystal) may be grown starting from a relatively imperfect, flawed crystal.

The value of such ruby crystals for the fabrication of solid optical masers (lasers) has recently been recognized. It is now becoming apparent for the first time, that the number of structural defects has a marked effect on the efficiency of such crystal lasers. Thus, a ruby produced by the above described invention will produce coherent light at a greater intensity than will the similar size ruby which includes a greater number of flaws, grown by the flame fusion method.

Although the specific example mentioned above concerns rubies for optical masers, many materials may be prepared so as to form relatively flawless crystals by the

inventive method so as to produce crystals for different purposes. Thus, not only rubies, but the closely related sapphires may obviously be produced by the above method both for laser and other industrial and precious gem uses (i.e., jewelry). Similarly, emeralds may be produced for any of the above purposes, as may calcium tungstate. Additionally, other crystals including the aluminum or iron garnets may be produced as pure crystals by the inventive method.

Because of the possible variation in growth directions, number of growth steps, and the different conditions (including constituents and their percentages) which may be utilized in the invention to adapt it to different types of crystals requiring different degrees of flawlessness, the various control parameters can be varied in many ways. Therefore, the invention is not limited to the specific steps of the exemplary embodiments, but rather is defined by the scope of the appended claims.

We claim:

1. The method of growing a relatively flaw-free crystal from a seed crystal containing many flaws, comprising:

causing the growing along a first direction on said seed crystal a first crystal extension;

utilizing at least part of said first crystal extension as a seed in a second growth process to produce a second crystal extension thereon along a second crystal axis direction;

utilizing at least part of said second crystal extension as a seed in a third growth process to produce a third crystal extension along a third crystal axis direction;

at least one of said first, second and third crystal axis directions being different from the others.

2. The method of growing a relatively flaw-free crystal from a seed crystal and at the same time producing at least one reusable, relatively flawless seed crystal, comprising:

first causing the growing along a first direction on said seed crystal of a first crystal extension;

utilizing at least part of said first crystal extension as a seed to cause the growing of a second crystal extension thereon along a second crystal axis direction in a second growth step;

utilizing at least part of said second crystal extension as a seed in a third growth step to cause the growing of a third relatively flaw-free crystal extension along a third crystal axis direction;

at least one of said first, second and third crystal axis directions being different from each of the others;

and severing at least a part of said second crystal extension from said third crystal extension after said third growth step;

so that said severed second crystal extension part and any parts of said second crystal extension which were not used as a seed in said third growth step may be utilized to produce additional relatively flaw-free crystals by means of a single-step growth process corresponding to said third growth step.

3. The method according to claim 6 in which:

of those dimensions of said third crystal extension which are parallel to both one of its surfaces and at least one of its edges, one dimension is at least as long as any of the other said dimensions;

and at least two of said first, second and third crystal axis directions along which growth occurs are at a substantial angle to said one long dimension of said third crystal extension,

whereby repetition of growth steps in directions along said one long dimension is avoided, and relatively large volumes of crystal extensions are grown relative to the various growth depth along said axis directions in at least two of said growth steps.

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