

[54] **CRUCIBLE**

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[22] Filed: **Jan. 3, 1972**

[21] Appl. No.: **215,229**

Related U.S. Application Data

[62] Division of Ser. No. 627,355, March 31, 1967, Pat.
No. 3,649,552.

[52] U.S. Cl. **23/292**, 23/273 R, 23/277 R,
164/60, 432/263, 266/39, 23/252 A, 423/489

[51] Int. Cl. **B011 3/04**

[58] Field of Search 23/277 R, 273 R, 301 SP,
23/273 SP, 292; 148/15, 16; 164/60;
432/263; 266/34 V, 39

[56] **References Cited**

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OTHER PUBLICATIONS

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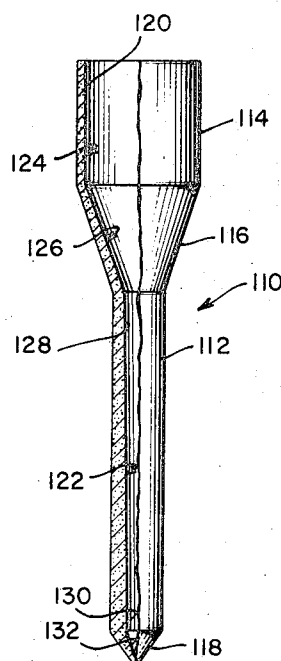
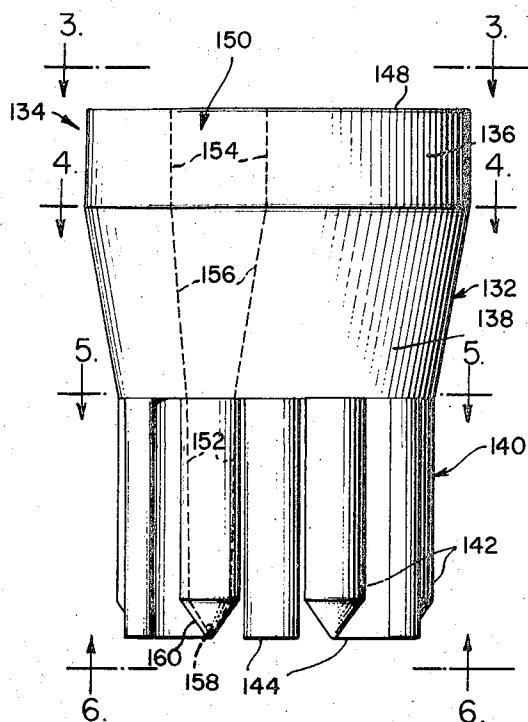
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[57]

ABSTRACT

The crucible is formed of compacted graphite or vitreous carbon and has an interior tapered toward its nucleation point. Single and multiport types are described for growing one or more crystals simultaneously. The crucible is useful for growing laser quality crystals of alkaline earth and rare earth fluorides, including mixed rare earth fluorides and mixed rare earth-alkaline earth fluorides which are free from oxides and oxyfluorides.

7 Claims, 8 Drawing Figures



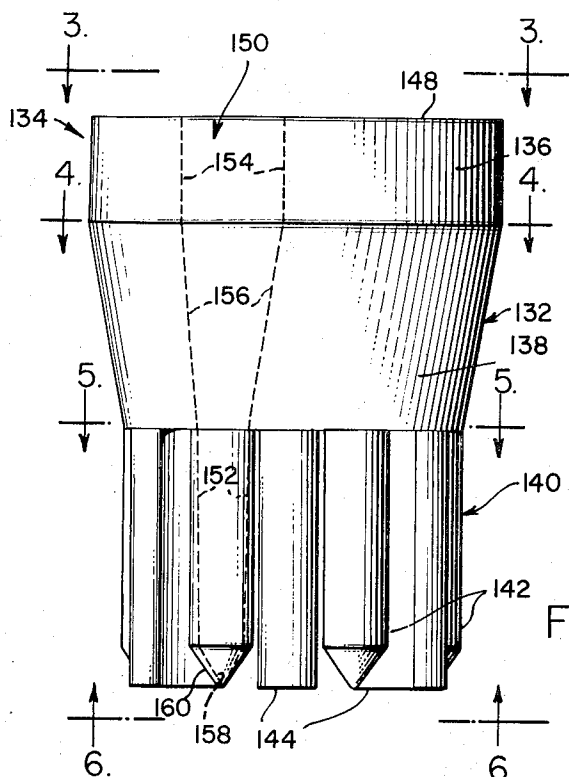


Fig. 2.

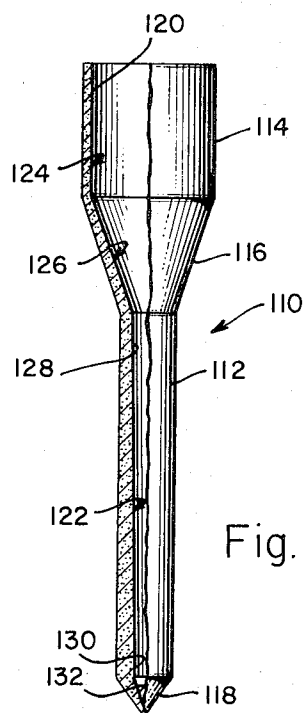


Fig. 1.

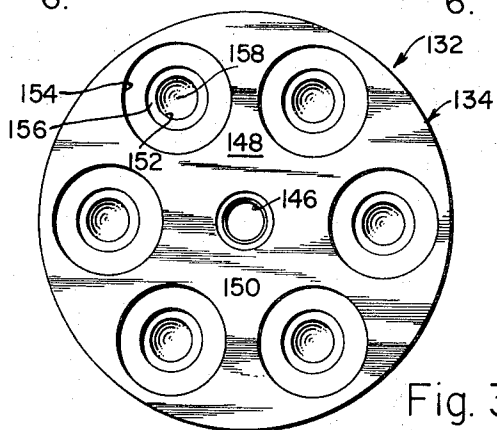


Fig. 3.

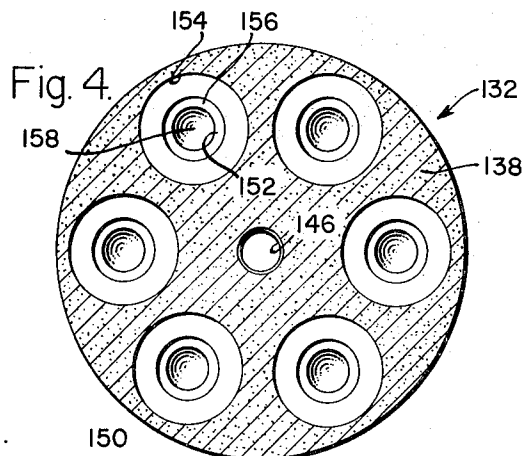


Fig. 4.

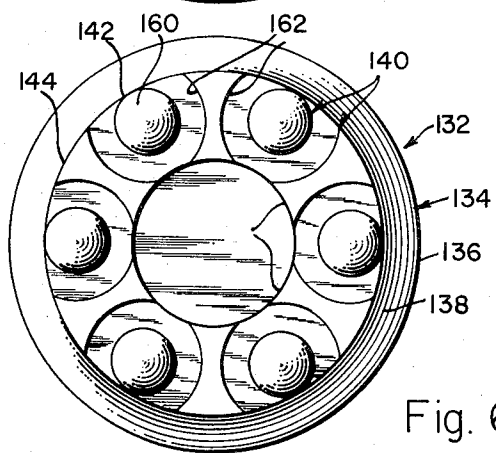


Fig. 6.

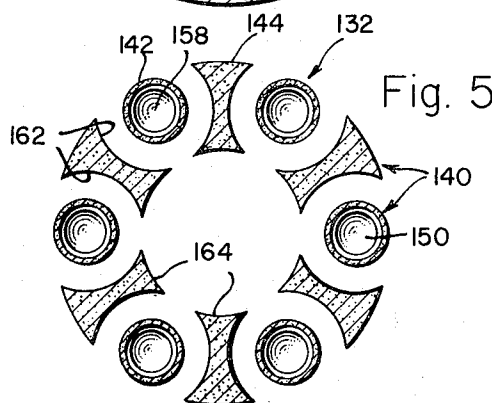


Fig. 5.

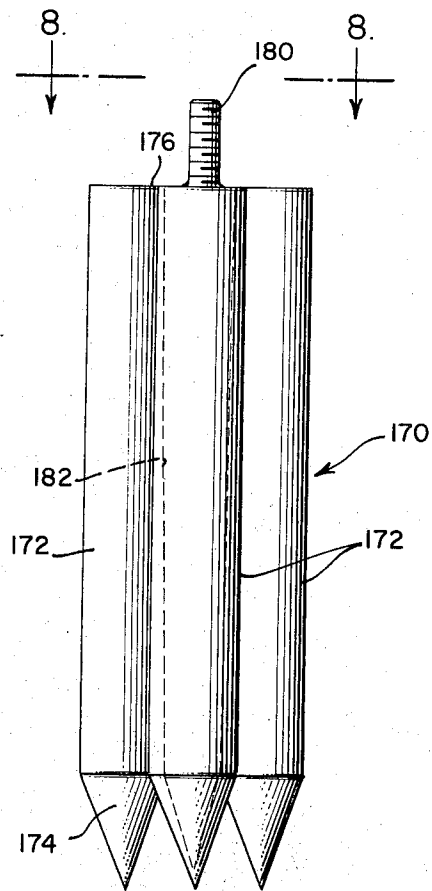


Fig. 7.

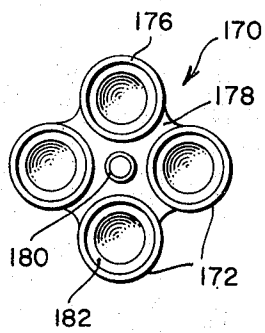


Fig. 8.

CRUCIBLE

CROSS-REFERENCE TO RELATED APPLICATION

This is a division of application Ser. No. 627,355, filed March 31, 1967, now U.S. Pat. No. 3,649,552 patented March 14, 1972.

BACKGROUND OF THE INVENTION

The present invention relates to a crucible for growing crystals. It is specifically useful in the preparation of optically pure crystals of alkaline earth and rare earth fluorides, including mixed rare earth fluorides and mixed rare earth-alkaline earth fluorides of laser quality free from oxides and oxyfluorides.

Laser devices require the use of crystals which are of ultra-high optical purity since even minute impurities cause internal scatter and opaqueness in the crystal, thereby preventing the desired light amplification. In recent years, interest has centered on crystals doped with rare earths since the rare earths possess qualities which are well-suited for laser studies. However, optical-grade fluoride single crystals, especially rare earth fluoride single crystal hosts doped with rare earth ions, have been particularly difficult to grow by prior art methods (see, for example, J. Czocharlski, *Z. Physik Chem.*, Vol. 92, p. 219 (1918); D. C. Stockbarger, *Journal of the Optical Society of America*, Vol. 39, p. 731 (1949); H. Guggenheim, *Journal of Applied Physics*, Vol. 34, No. 8, pp. 2482 - 2485, August, 1963).

PRIOR ART

Methods of growing crystals have been limited in that only one crystal at a time could be grown. Because the growth of high quality crystals is markedly dependent upon temperature and uniformity of temperature within the crystal, the time for growing a single crystal encompassed a period of time which can easily extend from a few days to as much as a few weeks. Consequently, it has not been previously possible to obtain a large quantity production of crystals in the absence of a large number of furnaces in which the crystals may be grown. It is obvious, therefore, that the growth of a large number of crystals required a correspondingly large investment in process equipment.

Furthermore, the crucibles used in prior processes to form such crystals as laser crystals were formed for platinum or platinum lined with carbon. When a platinum crucible is used, the formed crystal adheres to the platinum which requires that the crucible be torn away from the crystal so that the crystal may be obtained. Thus, such a crucible becomes unusable for further growth. When carbon is used as a liner for a platinum crucible and is exposed to such corrosive gasses as hydrogen fluoride, a reaction occurs at elevated temperatures to cause a diffusion of the carbon through the platinum. The platinum becomes brittle although the fluoride crystal is not contaminated; however, the lifetime of the platinum with its carbon liner is shortened. Furthermore, many prior processes utilized a closed crucible in which the crystal material and ambient atmosphere are contained so that, if the ambient atmosphere included hydrogen fluoride, noxious fumes would not escape therefrom. However, when the crystal was formed, the crucible had to be destroyed in order to remove the crystal.

SUMMARY OF THE INVENTION

The present invention overcomes these and other problems also by providing a very simple process means wherein a multiplicity of quality crystals may be formed at the same time.

In the growth of a crystal, a starting material may be loaded into a crucible which is formed with an open end. The crucible with the starting material therein is attached to a lowering rod in a crystal growth furnace and the temperature of the furnace is slowly raised in a desired atmosphere above the melting point of the material to produce melt.

The crucible is so constructed as to aid contact of the atmosphere with the melt, if needed. The crucible is then lowered at a rate commensurate with the growth rate of the crystal. At the end of the growth travel region, crystal annealing usually takes place. The time required for satisfactory annealing depends on the crystal material and the crucible material as well as the length and diameter of the crystal. The crystal is slowly cooled to a specified temperature, and the furnace is cooled to room temperature over a suitable period of time.

Preferably, when used to grow the fluoride crystals, the crucibles are made from graphite since neither a fluoride melt nor hydrogen fluoride atmosphere affects it. Other advantages of graphite are that the fluorides do not wet the graphite thus facilitating removal of the crystal from the crucible and that the graphite is of sufficient mechanical stability so that no fine graphite materials are transferred as impurities to the crystal. The crucibles are formed with one or more ports so that one or more crystals may be grown singly or simultaneously. Each port is closed at its bottom end and open at its upper end. The diameter of each port is greatest at its open end and decreases toward its closed end where it terminates at a point to facilitate nucleation of a single crystal. The decreasing diameter, in conjunction with the non-wetting characteristic of graphite, permits easy removal of the crystal grown. The decreasing diameter also acts as a funnel to increase contact of hydrogen fluoride with the melt. It is to be understood, however, that the graphite crucibles will facilitate removal of crystals regardless of the particular method of halide crystal growth employed.

Any suitable furnace may be used for crystal growth.

Other aims and objects, as well as a more complete understanding of the present invention will appear from the following explanation of exemplary embodiments and the accompanying drawings thereof, in which:

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a side elevational view, partly in section, of a single port crucible for growing a single crystal;

FIG. 2 is a side elevational view of a multiport crucible for growing simultaneously several crystals;

FIG. 3 is a top view, taken along lines 3-3 of FIG. 2, of the multiport crucible;

FIG. 4 is a sectional view, taken along lines 4-4 of FIG. 2, of the multiport crucible;

FIG. 5 is a sectional view, taken along lines 5-5 of FIG. 2, of the multiport crystal;

FIG. 6 is a bottom view, taken along lines 6-6 of FIG. 2, of the multiport crucible;

FIG. 7 is a side elevational view of a second multiport crucible for growing several crystals simultaneously; and

FIG. 8 is a view, taken along lines 8—8 of FIG. 7, of the second embodiment of the multiport crucible.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

One use of the present invention is more fully described in the above-noted U.S. Pat. No. 3,649,552.

The crucibles are formed entirely for vitreous carbon or a compacted graphite since neither the corrosive nature of a fluoride melt nor a hydrogen fluoride atmosphere affects the graphite. In addition, the fluorides do not wet the graphite, thus making the removal of the product quite easy. Furthermore, carbon has a melting point which is at least twice that of any of the crystals made by the inventive method and is insoluble therein. The graphite crucibles additionally have good thermal characteristics such that the heat of the furnace may be applied uniformly throughout the crystals during their growth. The graphite crucibles are relatively inexpensive, are easily machinable, and tend to resist shock. It is in part for these reasons that it is possible to form multiport crucibles so that several crystals may be grown simultaneously.

A single port crucible 110 is depicted in FIG. 1 and comprises a tubular portion 112, an entry portion 114, and an intermediate portion 116. Tubular portion 112 terminates in a point 118 for closure thereof. The crucible is provided with a bore 120 which varies according to the particular portion to form inner walls 122, 124 and 126, respectively, of tubular portion 112, entry portion 114 and intermediate portion 116. Inner wall 112 of portion 112 is provided with a diameter at its upper end 128 which is greater than the diameter at its lower end 130. Thus, inner wall 122 tapers from its upper end to its lower end. Inner wall 132 of point 118 converges to a point from lower end 130 of portion 122 to serve as a nucleation point by which growth of a single crystal may be accomplished. Inner wall 124 of portion 114 is cylindrical and is provided with a diameter which is relatively larger than the diameter of walls 126 and 122. Inner wall 126 of portion 116 converges from inner wall 124 to the upper end 128 of inner wall 122 thus providing a gentle taper of bore 120.

Referring now to FIGS. 1-6, a multiport crucible 132 comprises a solid upper section 134, having an entry portion 136 and an intermediate portion 138, and a lower section 140 having tubular portions 142 and fins 144. Entry portion 136 is provided with an outer diameter which is greater than that of lower section 140 and intermediate portion 138 has an outer diameter which tapers from that of portion 136 to that of section 140. A tapped and internally threaded connecting means 146 is centrally disposed within entry portion 136 and crucible 132 and forms an opening in upper face 148 of portion 136. An externally threaded rod is adapted to threadedly engage crucible 132 within connecting means 146 to enable the positioning and movement of the multiport crucible within a crystal growing furnace.

As depicted in FIGS. 2-6, crucible 132 is adapted to permit simultaneous growth of six crystals in six individual components 150 of crucible 132. The internal construction of each component 150 is similar to that as illustrated with respect to FIG. 1 in such a manner

that each tubular portion 142 is provided with an inner wall 152 which tapers from its upper end toward its lower end, entry portion 136 is provided with an inner cylindrical wall 154 and intermediate portion 138 is provided with a tapered inner wall 156 which joins inner wall 154 with the upper end of inner wall 152. The lower end of inner wall 152 converges to a nucleation point 158 within a point 160 of tubular portion 142.

Fins 144 extend downwardly from intermediate portion 138 and are formed with curved surfaces 162, as best seen in FIGS. 5 and 6, which are spaced from but concentric with tubular portion 142. Fins 144 are used to add support to crucible 132, to protect points 160 of tubular portions 142, and to prevent dissipation of heat from the tubular portions so that the growth and the stability of the crystals will be enhanced. A circular output 164, concentric with the axis of crucible 132, is placed interior to tubular portions 142 and fins 144 to permit even distribution of heat to the crystals during the time of their formation.

A third embodiment (see FIGS. 7 and 8) comprises a multiport crucible 170 including four tubular components 172 having pointed extremities 174 at one end thereof and entry portions 176 at the other extremity thereof. Components 172 are joined at their upper ends by a web 178 (see FIG. 8) and a threaded nipple 180 extends from web 178 for engagement with a rod. The inner walls 182 of each of the tubular components 172 are similar to inner wall 122 of tubular portion 112, as depicted in FIG. 1.

In all cases, those inner walls which are in contact with the crystal are tapered in order to facilitate removal of the crystal after having been grown without necessitating the destruction of the crucible.

Although the invention has been described with reference to particular embodiments thereof, it should be realized that various changes and modifications may be made therein without departing from the spirit and scope of the invention.

What is claimed is:

1. A crucible for growing crystals from starting materials comprising an elongate tube for receiving the starting materials and having:

internal bore means bounded at both ends by means defining openings, said opening means at a first of said ends being larger in dimension than the opening means at a second of said ends to provide said bore means with a taper decreasing from said first end to said second end; and
a closed tapered pointed end at and terminating said second end of said bore means.

2. A crucible as in claim 1 further including an entry portion provided with opening means of greater dimension than that of said bore means at said first end and a connecting portion secured between said entry portion and said tube at said first end, said connecting portion having a tapered bore diminishing in dimension from the entry portion bore to the first end.

3. A crucible as in claim 1 wherein said tube is constructed of compacted graphite.

4. A multiport crucible for simultaneously processing several crystals including a plurality of elongate tubes for each of the several crystals, each said tube having internal bore means bounded by first and second open portions, and a closed pointed end terminating said second open portion, said bore means of each said tube

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being of greater dimension at said first open portion than at said second open portion to form a taper in said bore means, and means securing said tubes together at said first open portions.

5. A crucible as in claim 4 further including an entry section having a plurality of entry ports, each of said ports having a dimension greater than that of each of said first open portions, and passage means connected

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between said entry ports and said first open portions.

6. A crucible as in claim 5 further including a plurality of fins secured to said entry section and partially enclosing said tubes.

7. A crucible as in claim 6 formed from compacted graphite.

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