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APPARATUS FOR GROWING FLUORIDE CRYSTALS

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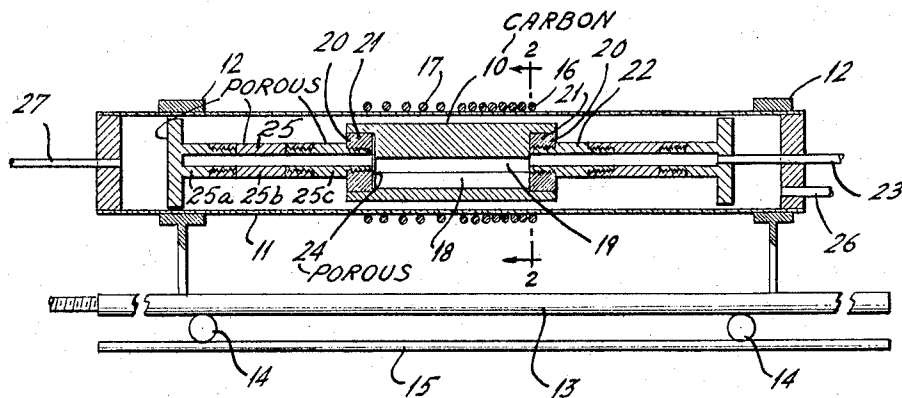


FIG. 1.

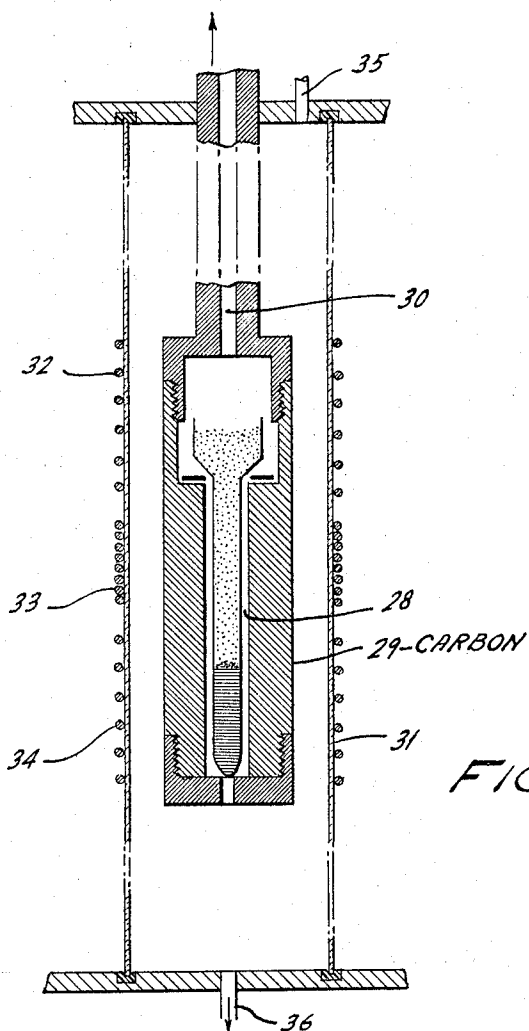
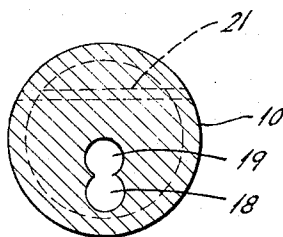


FIG. 3.

FIG. 2.



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APPARATUS FOR GROWING FLUORIDE CRYSTALS

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8 Claims. (Cl. 23—273)

This invention relates to the growing of fluoride crystals, such as lanthanum fluoride crystals, which are useful in laser applications.

In the growing of such crystals, it is necessary to exclude oxygen and water vapor because oxides have adverse effects upon the optical properties of the crystals. For this reason such crystals are grown in a reactive gas ambient. At the present time the preferred reactive gas is hydrogen fluoride which not only excludes oxygen and water vapor but also converts any metal oxides to fluorides at the operating temperatures.

The principal object of the present invention is to provide improved apparatus for growing fluoride crystals.

Another object of the invention is to provide such an apparatus wherein inner and outer chambers are employed and different gases are supplied thereto for the purposes hereinafter set forth.

Other objects of the invention will become apparent as the description proceeds.

A feature of the invention is the provision of apparatus comprising inner and outer chambers wherein the inner chamber is employed as the crystal-growing chamber to which a reactive gas is supplied as an ambient for the crystal growth, and an inert gas is caused to flow continuously through the outer chamber to protect the inner chamber.

Another feature of the invention is the provision of dual-chamber apparatus in which the inner chamber is formed of porous material, reactive gas is supplied to the crystal-growing chamber and the excess of said gas diffuses into the other chamber, and an inert gas is caused to flow continuously through said other chamber to carry away the reactive gas.

Still another feature of the invention is the provision of a horizontal type of apparatus employing a special form of crystal-growing chamber or crucible.

The invention may be fully understood from the following detailed description with reference to the accompanying drawing wherein

FIG. 1 is a longitudinal sectional view of a horizontal form of the apparatus according to this invention;

FIG. 2 is a cross-sectional view taken along line 2—2 in FIG. 1; and

FIG. 3 is a longitudinal sectional view of a vertical form of the apparatus according to the invention.

Referring first to FIG. 1 of the drawing, the apparatus shown comprises a cylindrical inner chamber or crucible 10 disposed within an outer cylindrical chamber 11 which is supported by clamp rings 12 on a movable carriage 13 which has rollers 14 engaging tracks 15. The assembly comprising the two chambers is movable from right to left, in relation to stationary RF heating coils 16 and 17, by any suitable means (not shown) such as a variable speed motor and a speed reduction drive, it being understood that the movement of the assembly is quite slow.

As shown in FIGS. 1 and 2, the inner chamber 10, which is formed of porous material such as carbon, is specially designed to subject a crystal growing therein to thermal gradients. The crystal-growing cavity 18 is eccentrically positioned so as to make the wall of the chamber or crucible thin at the bottom and of increasing thickness toward the top. Since the thicker sections retain more heat than the thin section at the bottom, the

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cooling of the solidifying crystal starts at the bottom and the crystal is subjected to thermal gradients. This promotes upward expulsion of gas bubbles from the solidifying crystal, relieving strain and preventing cracking.

The crystal-growing cavity 18 is in communication with a loading cavity 19 through which the material for crystal growth together with a dopant may be loaded into cavity 18. In the case of lanthanum fluoride, the dopant may be trivalent neodymium or any other rare earth metal ion.

Recessed in the ends of chamber 10 are end pieces 20 which are held by pins 21. Connected to the right-hand end is a gas inlet tube 22 to which a reactive gas, preferably hydrogen fluoride gas, is supplied through a supply tube 23 under predetermined pressure and rate of flow.

The opposite end of chamber 10 is closed by a thin porous plate 24 which may be composed of carbon. Connected to the same end of chamber 10 is a porous tubular section 25 which may also be composed of carbon. In the illustrated structure the tubular section 25 is comprised of threadedly-connected elements 25a, 25b and 25c, all of which may be composed of carbon.

The outer chamber 11 may be formed of quartz. Connected to the ends thereof are inlet tube 26 and outlet tube 27. An inert gas, such as argon, is supplied under predetermined pressure and rate of flow to chamber 11 through tube 26 and leaves chamber 11 through the outlet tube 27.

In operation the crystal growth in cavity 18 is effected in known manner by subjecting the material therein successively to melting and annealing temperatures. The carbon chamber 10 is heated by induction first to high temperature by coil 16 and then to lower temperature by coil 17. The reactive gas, which is preferably hydrogen fluoride gas, is supplied under preadjusted pressure to the inner chamber 10 as an ambient for crystal growth. This gas reacts with oxygen compounds in the starting material and displaces the oxygen. It also prevents further oxidation of the material by absorbed oxygen. The excess of this gas and the gaseous reaction products diffuse through the porous thin wall section of the inner chamber 10 into the outer chamber 11, and it also diffuses through plate 24 and section 25 to the outer chamber, thus providing a controlled slow flow rate for the reactive gas. At the same time, inert gas (e.g. argon) is caused to flow under pressure through the outer chamber. This gas carries away the reactive gas and it also protects the inner chamber. The exhausted gas can be disposed of in any suitable manner. It can be exhausted into the atmosphere or into a large vessel where the hydrogen fluoride can be neutralized.

In this apparatus, the inner chamber 10 serves as a heat source, crucible, and atmosphere container simultaneously. The crystal growth takes place in a continuously moving ambient gas which is expelled by diffusion into the outer chamber and is then carried away by the flushing inert gas. Experimentation has shown that this apparatus is capable of producing excellent crystals.

Referring now to FIG. 3, there is shown a vertical form of the apparatus in which the materials are placed in a tube 28 which is supported within chamber 29. Reactive gas, which is preferably hydrogen fluoride, is supplied under predetermined pressure to chamber 29 through inlet 30. The apparatus also comprises outer chamber 31 and RF heating coils, 32, 33 and 34. Inert gas, such as argon, is supplied under predetermined pressure to chamber 31 through inlet 35 and is expelled through outlet 36. Chamber 29 is movable vertically in relation to chamber 31 and the heating coils which are stationary.

In operation chamber 29 is lowered slowly by suitable lowering mechanism to subject the crystal-growing material first to preheating temperature by coil 32, then to

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melting temperature by coil 33, and then annealing temperature by coil 34.

While certain embodiments of the invention have been shown and described, it will be understood that the invention is not limited thereto but contemplates such modifications and further embodiments as may occur to those skilled in the art.

I claim:

1. In an apparatus for growing fluoride crystals, a horizontally-movable assembly comprising a horizontally-disposed porous-walled crystal-growing inner chamber and a similarly-disposed outer chamber, stationary heating means outside said outer chamber to effect crystal growth in said inner chamber as said assembly is moved, means for introducing reactive gas into said inner chamber as an ambient for the crystal growth, the porosity of said inner chamber permitting the excess of said gas to diffuse through the wall of the inner chamber into the outer chamber, and means for separately introducing and continuously flowing an inert gas into and through said outer chamber to protect said inner chamber and to carry away the reactive gas that has entered the outer chamber.

2. In an apparatus for growing fluoride crystals, an inner porous-walled chamber in which the crystal growth takes place, means for supplying heat to said chamber, means for introducing reactive gas into said chamber as an ambient for the crystal growth, an outer chamber into which excess of said gas passes by diffusion through the porous wall of said inner chamber, and means comprising inlet and outlet tubes connected to said outer chamber for separately introducing and continuously flowing an inert gas into and through said outer chamber to carry away the reactive gas and to protect the inner chamber.

3. Apparatus according to claim 2, wherein said inner chamber has a thin wall bottom section and thicker wall sections thereabove to subject the growing crystal to thermal gradients.

4. Apparatus according to claim 4, wherein said inner chamber is of cylindrical form and has an eccentrically positioned crystal-growing cavity to provide thin and thick wall sections and thus subject the growing crystal to thermal gradients.

5. An apparatus according to claim 1, wherein the reactive gas is introduced into one end of said inner cham-

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ber, and the opposite end of said inner chamber is closed by a thin porous plate through which said reactive gas may diffuse.

6. An apparatus according to claim 5, wherein a porous tubular section is connected to said opposite end of said inner chamber, through which tubular section said reactive gas may diffuse.

7. In an apparatus for growing fluoride crystals, a movable porous-walled inner chamber in which the crystal growth takes place, a stationary outer chamber, stationary heating coils outside said outer chamber to effect crystal growth in said inner chamber as the latter is moved, means for introducing reactive gas into said inner chamber as an ambient for the crystal growth, the porosity of said inner chamber permitting the excess of said gas to diffuse through the wall of the inner chamber into said outer chamber, and means for separately introducing and continuously flowing an inert gas into and through said outer chamber to carry away the reactive gas and to protect the inner chamber.

8. In an apparatus for growing fluoride crystals, an inner porous-walled chamber in which the crystal growth takes place, an outer chamber, heating means outside said outer chamber, means for introducing reactive gas into said inner chamber as an ambient for the crystal growth, the porosity of said inner chamber permitting the excess of said gas to diffuse through the wall of the inner chamber into said outer chamber, and means comprising inlet and outlet tubes connected to said outer chamber for separately introducing and continuously flowing an inert gas into and through said outer chamber to carry away the reactive gas and to protect the inner chamber.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,273,969

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It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 38, for claim reference numeral "4" read
-- 3 --.

Signed and sealed this 29th day of August 1967.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWARD J. BRENNER

Commissioner of Patents