

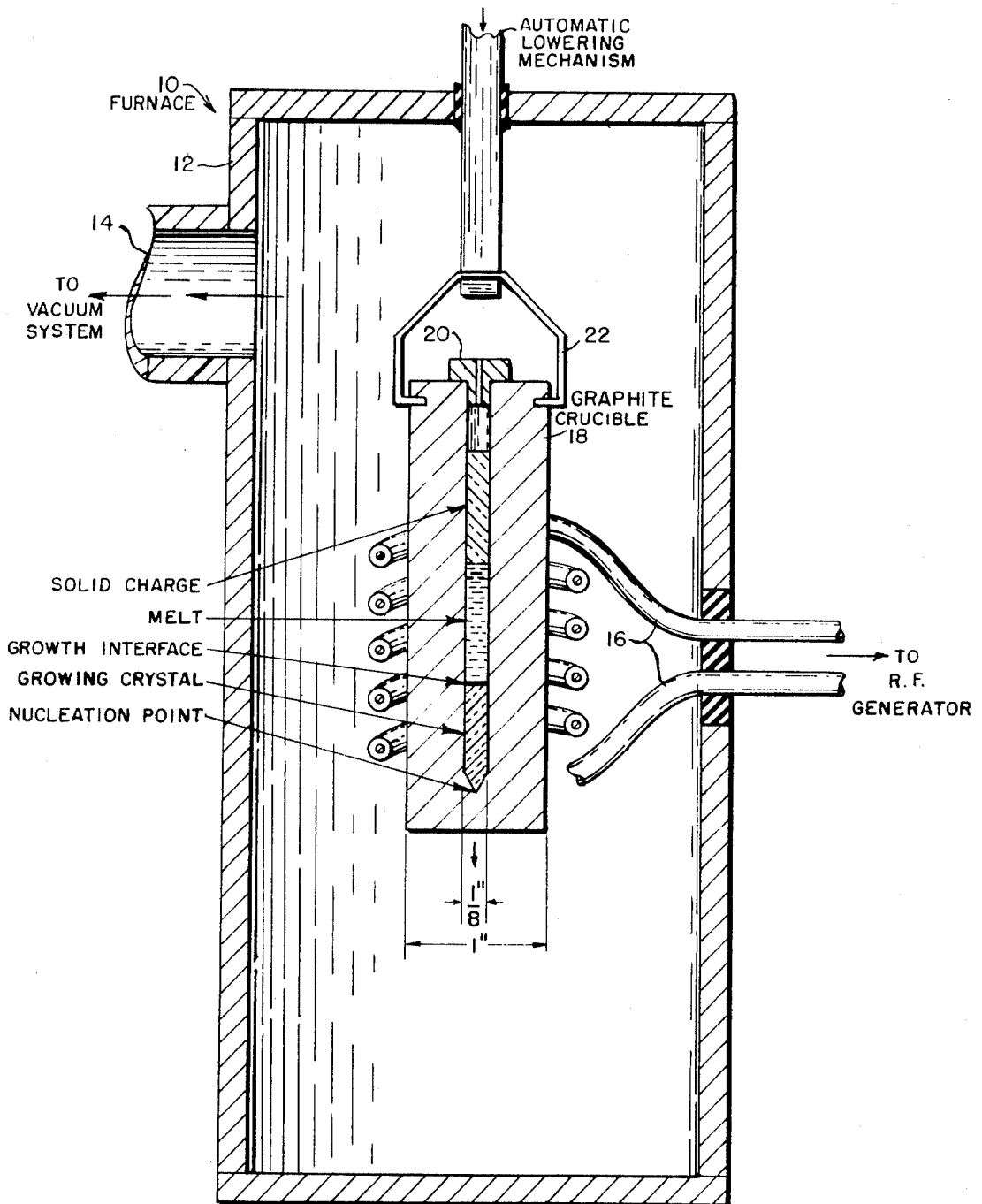
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METHOD OF GROWING STRAIN-FREE SINGLE CRYSTALS

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3,514,265 METHOD OF GROWING STRAIN-FREE SINGLE CRYSTALS

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ABSTRACT OF THE DISCLOSURE

Small diameter, strain-free single crystals are grown from a melt of powder in a high density crucible having a high ratio of outer diameter to inner diameter by gradually lowering the crucible through an RF coil contained in an evacuated furnace.

BACKGROUND OF THE INVENTION

This invention relates in general to a method of growing strain-free single crystals, and in particular to a method of growing strain-free small diameter single crystals in laser rod form.

Low threshold laser crystals must be highly perfect and strain free. For continuous wave operation, further threshold lowering and more effective cooling is achieved by the use of small diameter crystals. A method presently used for the production of laser rods involves the growth of a large diameter crystal which is slowly grown over a period of many hours, cooled very slowly, annealed for days in special ambients to remove growth-induced strains, and finally machined to size. Such rods are still prone to fracture because of residual strain during the initial cool-down prior to laser oscillation tests.

SUMMARY OF THE INVENTION

The general object of this invention is to provide a method of growing a small diameter strain-free single crystal. A particular object of this invention is to provide a method of growing these single crystals in laser rod form. A still further object of this invention is to provide a method of growing a small diameter strain-free single crystal which eliminates the time consuming requirement of annealing or after heating, necessary in conventional growth methods.

It has now been found that the foregoing objectives can be attained by a method utilizing a high density, high purity crucible as hereinafter more fully described. According to the invention, a high density, high purity crucible is filled with the powder to be grown. The filled crucible is then capped with a vented plug and positioned within an RF heating coil contained in an evacuated furnace. The powder is melted and the temperature increased to establish thermal equilibrium. Crystal growth is then started by lowering the crucible through the RF coil at a prescribed rate, the lowering of the crucible being stopped after the melt has crystallized.

The invention can be best understood by referring to the accompanying drawing wherein there is shown a cross section of suitable apparatus for carrying out the invention.

BRIEF DESCRIPTION OF THE DRAWING

Referring to the drawing, a furnace 10 is fitted with a water cooled jacket 12 and evacuating means 14. Positioned within the furnace 10 in approximately the center thereof is a water cooled RF coil 16. A high density, high purity crucible 18 capped with a vented plug 20 is hung by crucible hanger 22 in such manner as to be passable through RF coil 16, as shown. An automatic

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lowering mechanism (indicated by the arrow) is operatively connected with crucible hanger 22 and serves to lower the crucible 18 through the RF coil 16.

DESCRIPTION OF THE PREFERRED EMBODIMENT

In a specific embodiment of the invention, a high density, high purity graphite crucible 18 having an outer diameter of about one inch and an inner diameter of about $\frac{1}{8}$ inch to form a bore is filled with a mixture of calcium fluoride powder or cadmium fluoride powder with 0.1 mole percent by weight of the total mix of dysprosium fluoride. The crucible bore is then capped with a vented plug 20 to reduce the escape of calcium fluoride vapors and the entire assembly is placed in furnace 10 substantially as shown, the furnace being evacuated to 10^{-5} to 10^{-6} torr. After the charge has been melted, the temperature is increased another 100° C. After thermal equilibrium is established, the growth of a single crystal is started by lowering the crucible through the RF coil 16 at a rate of about $\frac{1}{8}$ inch to about $\frac{3}{4}$ inch per hour. As shown, nucleation occurs at a point below RF coil 16. After the melt has crystallized, the lowering of the crucible 18 is stopped. The temperature of the grown single crystal is decreased from the melting point to 300° C. by increments of about 100° C. per 5 minutes to eliminate the occurrence of strain in the last solidified portion of the crystal; then all power to the RF coil 16 is turned off. After two hours the furnace 10 is blanked off from the vacuum system 14 and the crucible is cooled at room temperature before its removal. The crystal is then easily freed from the crucible by gentle tapping.

In the method as described above, the thick walled graphite crucible provides a large thermal mass which allows sudden fluctuations of energy input (due to line voltage variations) to be damped out before their effect can reach the growing crystal. The large thermal mass and the low thermal conductivity of the graphite crucible, in addition to the small crystal diameter, allow a planar growth interface which is the ideal situation for growth of single crystals. During growth, as any plane of the crucible passes through the RF coil, it continues to be heated by the RF field. As the flux lines fan out rapidly, the heating of the crucible tapers off gradually away from the coil. This tapering heat input helps to balance the radiative loss and produces a gradual, instead of an abrupt, temperature change in the crystal beyond the recrystallization isotherm. This "residual" RF heating, the large thermal mass, and low thermal conductivity of the thick wall graphite all contribute to the very gradual temperature change along the crucible. The very gradual temperature decrease along the crucible means that the isotherms are perpendicular to the crucible axis and decrease in temperature away from the RF heater. As a result, the radial heat loss from the crystal is almost eliminated and the major heat flow from the crystal is essentially in an axial direction away from the growth interface. This one dimensional distribution of heat has been shown to be the most desirable condition for cooling a grown crystal. The beneficial effect of the method of the invention is verified by substituting a thin-wall graphite crucible for the thick wall and keeping all other parameters constant for a growth run. Though the crystals grown in the thin-wall crucible are predominantly single, none are strain free.

The single crystals are grown according to the invention in a matter of hours. Except for cutting and polishing of the ends, they are in laser rod form. For growth of other compounds or elements, a crucible of suitable RF susceptor type material and appropriate ambient are

chosen. The length of the particular crucible used depends upon the length of the crystal desired and the limitations of the growth apparatus. The ratio of the outer diameter to the inner diameter of the particular crucible used should be at least 8 to 1. Of course, the crucible used must not react with the material that you are attempting to grow and must not stick to it after freezing.

Then, too, rather than cool the crystal by the 100° C. per 5 minute increments as shown in the embodiment, a more favorable method would be an automatic and continuous temperature decrease over a specified period of time. The ideal case, if furnace dimensions allowed, would be to have a crucible of sufficient length, possibly 24 inches, with the crystal in the bottom lowered three inches through the RF coil until the top of the grown crystal was at 300° C. or less. Depending on the crystalline or amorphous material to be grown, an appropriate atmosphere is chosen, such as an inert gas or nitrogen. The RF coil can also be of sufficient length so that all the material not nucleated will be in a molten state.

Several methods were used to evaluate the quality and properties of the crystals grown. All cleaved easily on the {111} plane and resulted in flat surfaces free of curvature which is a good indication of the absence of strain. When the crystals were viewed through crossed polarizers no evidence of strain was seen.

The crystals were tested for lineage and singularity, by means of a scanning Laue X-ray diffraction method, in which the crystal and film are translated together normal to a stationary X-ray beam in the Laue arrangement. The resulting photograph shows a series of lines which are parallel to the direction of crystal translation. The straightness of these lines is a measure of the crystalline perfection. Imperfections such as lineage, mosaic structure, and grain boundaries, will be revealed as irregularities and breaks in the lines. Representative patterns show that the crystals grown by this technique have a high degree of perfection.

Dislocation counts for the unactivated crystals grown by this method were 5.3×10^4 /sq. cm. compared to 4×10^5 /sq. cm. for the optical grade CaF_2 (Harshaw Chemical Co.) starting material.

A $\text{CaF}_2:\text{Dy}^{3+}$ crystal, grown according to the invention, its ends paralleled, polished, and silvered, then irradiated with electrons to convert the Dy^{3+} to Dy^{2+} was tested for laser oscillations. The pulsed threshold for the crystal at 77° K. in a concentric head was 28 joules input to an T524 lamp.

Seeded $\langle 111 \rangle$ crystals have been grown by this method. The easy cleavage {111} plane is perpendicular to the crystal axis. Thus the ends of the crystal can be cleaved off easily with a razor blade resulting in a laser rod with a Fabry-Perot geometry.

Consequently a suitably activated crystal, with cleaved ends, mounted in an outside mirror type laser head can be used for laser oscillations almost upon removal from the growth crucible.

This would eliminate the many steps and many hours required for slow crystal growth, slow cooldown, anneal-

ing, paralleling and polishing the ends and polishing the barrel of the laser crystal.

The foregoing description is to be considered merely as illustrative of the invention and not in limitation thereof.

What is claimed is:

1. Method of growing small diameter strain-free single crystals including the steps of:

- (A) filling a high density, high purity graphite crucible having an outer diameter of about one inch and an inner diameter of about $\frac{1}{8}$ inch with a mixture of calcium fluoride with about 0.1 mole percent by weight of dysprosium fluoride,
- (B) capping the filled crucible with a vented plug,
- (C) positioning the filled crucible within an RF heating coil contained in an evacuated furnace,
- (D) melting the crystalline powder,
- (E) increasing the temperature to establish thermal equilibrium,
- (F) starting crystal growth by lowering the crucible through the RF coil at a rate of about $\frac{1}{8}$ inch to about $\frac{3}{4}$ inch per hour, and
- (G) stopping the lowering of the crucible after the melt has crystallized.

2. Method of growing small diameter strain-free single crystals including the steps of:

- (A) filling a high density, high purity graphite crucible having an outer diameter of about one inch and an inner diameter of about $\frac{1}{8}$ inch with a mixture of calcium fluoride with about 0.1 mole percent by weight of dysprosium fluoride,
- (B) capping the filled crucible with a vented plug,
- (C) positioning the filled crucible within an RF heating coil contained in an evacuated furnace,
- (D) melting the crystalline powder,
- (E) increasing the temperature to establish thermal equilibrium,
- (F) starting crystal growth by lowering the crucible through the RF coil at a rate of about $\frac{1}{8}$ inch to about $\frac{3}{4}$ inch per hour, and
- (G) stopping the lowering of the crucible after the melt has crystallized.

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