June 21, 1966 K. NASSAU 3,257,327

PROCESS FOR GROWING NEODYMIUM DOPED SINGLE CRYSTAL DIVALENT METAL ION TUNGSTATES

Filed May 7, 1962

FIG. 1

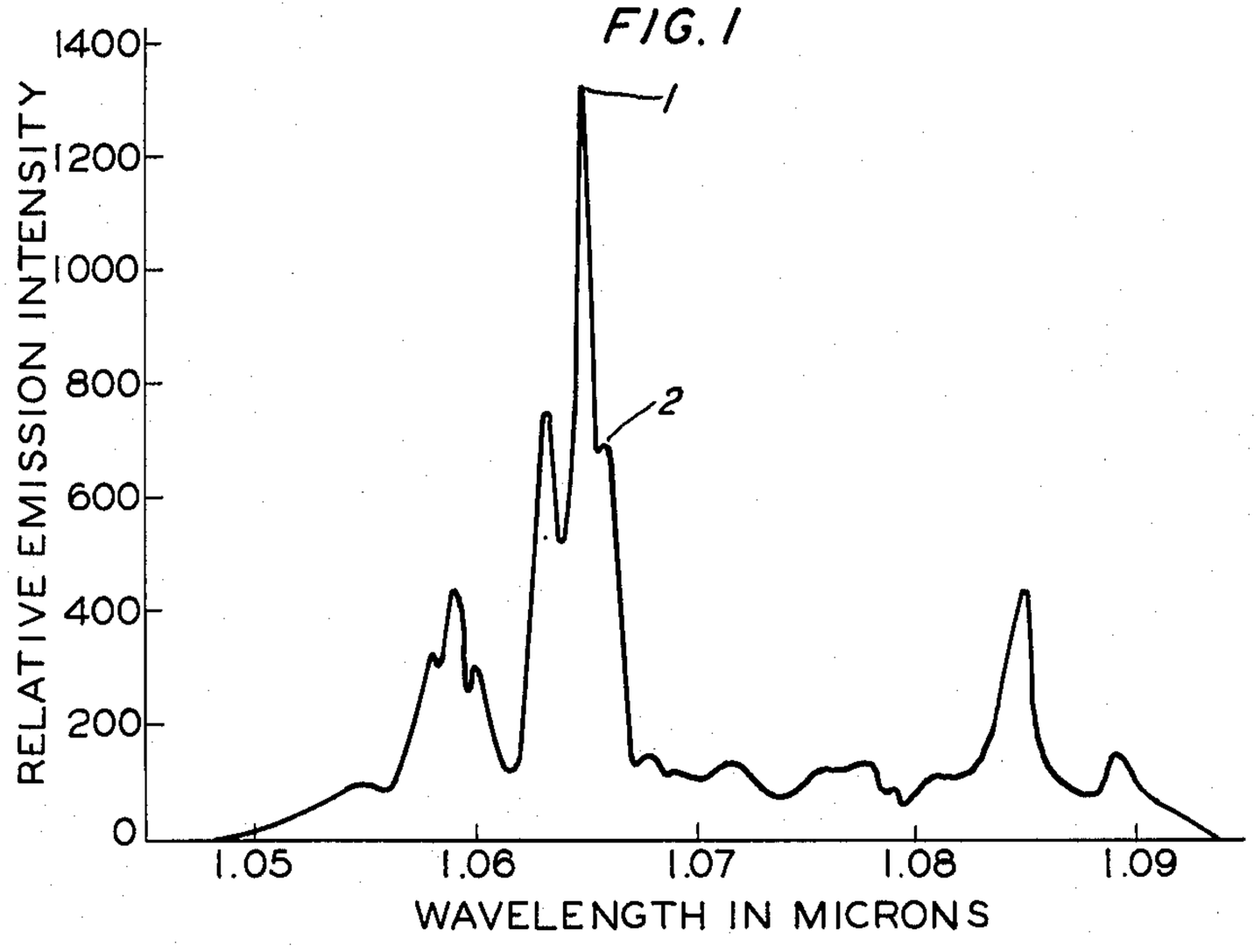
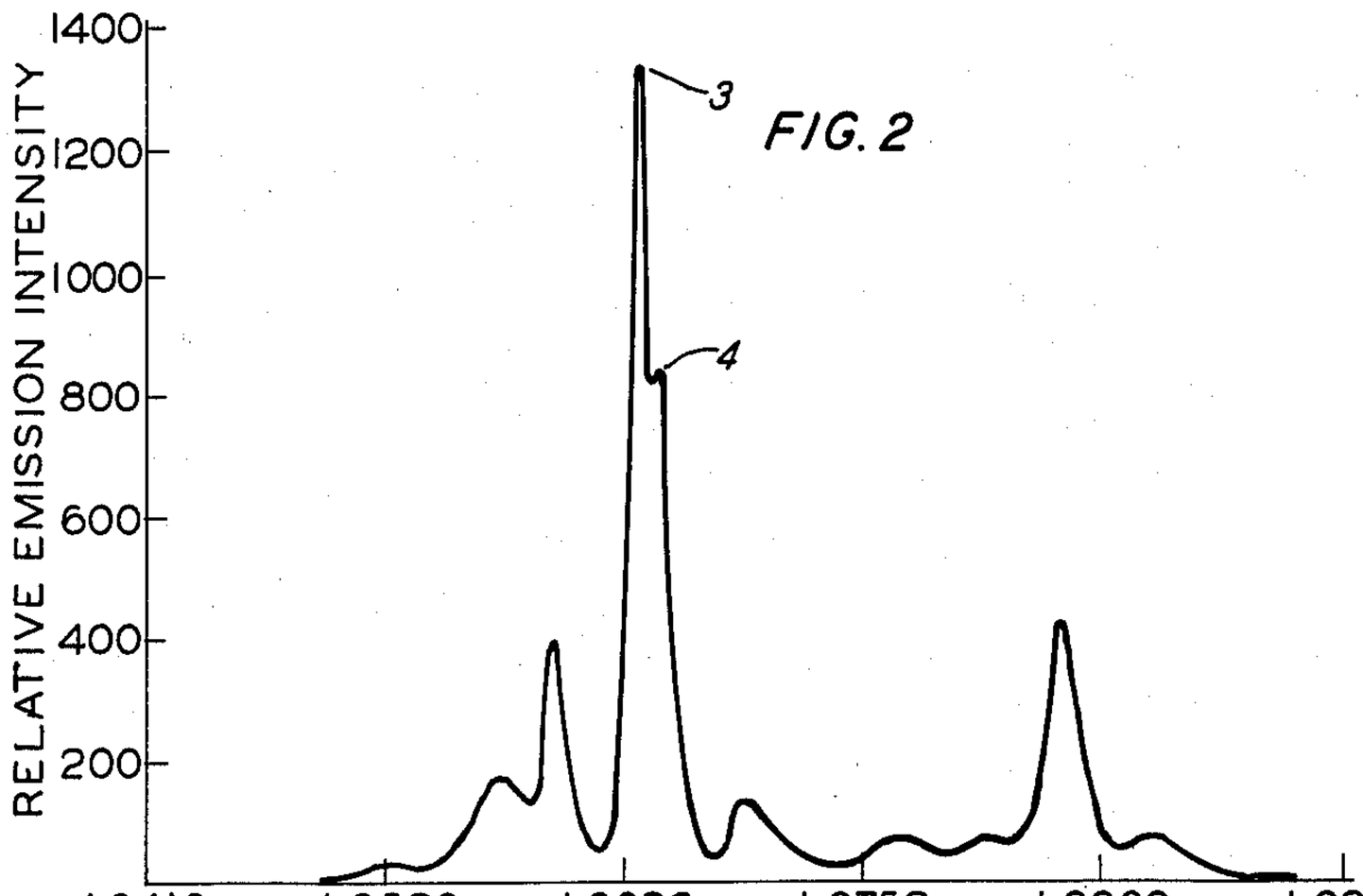


FIG. 2



INVENTOR
K. NASSAU
BY Richard H. Bryer
ATTORNEY

United States Patent Office

3,257,327

Patented June 21, 1966

3,257,327

PROCESS FOR GROWING NEODYMIUM DOPED SINGLE CRYSTAL DIVALENT METAL ION TUNGSTATES

Kurt Nassau, Springfield, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

Filed May 7, 1962, Ser. No. 192,723
3 Claims. (Cl. 252—301.5)

This invention relates to a method of growing single crystal tungstates containing small additions of monovalent and paramagnetic ions. and to crystals so grown.

In recent years there have been developed two classes of solid state maser devices, the microwave maser and the optical maser, in which electromagnetic wave energy amplification by stimulated emission of radiation occurs. The mechanics of microwave amplification are well detailed in the literature as, for example, in the article entitled "A Maser," page 18 of the Microwave Journal for November/December 1958, and the article entitled "A Solid-State Maser, a Supercooled Amplifier," page 16, Electronics, Engineering Edition, April 25, 1958. Devices in which the stimulated frequency is in the spectral range from far infrared to ultraviolet, encompassing the wavelength range of from 100 A. to 2×10^6 A., are termed optical masers and are directly analogous in operation to the microwave maser. One particular description of devices of this type is found in United States Patent 2,929,922 to Schawlow and Townes.

One of the more promising maser devices is that which utilizes as the active material a diamagnetic crystal containing small inclusions of trivalent rare earth ions from which the stimulated emission occurs. A class of diamagnetic crystals found to be particularly advantageous is the divalent metal ion tungstates having the Scheelite structure. Copending U.S. application Serial No. 139,266, filed September 15, 1961, describes an optical maser device utilizing neodymium-containing calcium tungstate crystals as the active maser material. United States Patent 3,003,112 to L. G. Van Uitert describes a microwave maser device wherein the active maser material is a divalent metal-ion tungstate containing various trivalent rare earth ions.

The tungstate crystals are conveniently made by a method described as the Czochralski method. This method is described in an article by J. Czochralski in Zeitschrift für Physikalische Chemie, volume 92, pages 219–221 (1918). A recent description of the process is found in an article by K. Nassau and L. G. Van Uitert in Journal of Applied Physics, volume 31, page 1508 (1960). In accordance with this method, a melt is formed of a mixture of initial ingredients, the composition of the melt controlling the composition of the grown crystal. A seed crystal is inserted into the melt and simultaneously rotated and slowly withdrawn therefrom, crystal growth being thereby promoted on the seed crystal.

The method has certain disadvantages, however, which have led to a continuing search by the art for improved processes for growing tungstate crystals. In particular, the distribution coefficient of the trivalent rare earth ions in the melt compared to those incorporated into the crystal during growth is very unfavorable. For one particular mateiral, calcium tungstate doped with nedoymium, the melt must contain one atom percent neodymium, based on the calcium ions present, in order to grow a crystal containing only 0.24 atom percent neodymium.

Further, as understood by the art, the absorption and emission spectra for trivalent rare earth ions in melt grown tungstates is not simple. Part of the complexity arises from the present of a trivolent ion in a divalent lattice.

The particular spectrum characteristic of the trivalent ion is dependent on the particular environment in which the ion is located in the tungstate crystalline lattice. Various permissible locations are available for the ion during crystal growth including one adjacent a divalent metal-ion vacancy, one adjacent another trivalent ion, one adjacent both a vacancy and another trivalet ion or one completely surrounded by divalent metal ions. Each particular ordering around the rare earth ion gives rise to a distinct series of absorption and emission lines. The resulting multiplicity of such lines dissipates power and detracts from the intensity of any one of them. Calcium tungstate doped with cerium, for example, has a plurality of paramagnetic resonance lines in the region $g=1.43$ to $g=2.92$. Calcium tungstate doped with neodymium has a plurality of fluorescent lines in the 0.8 to 1.4 micron region.

An additional disadvantage of these melt grown crystals is the limited number of input signal frequencies capable of being amplified. For a minimum power input to produce maser action, each trivalent rare earth ion emits energy in only one primary line. Since the number of trivalent rare earth ions possessing the requisite characteristics necessary for maser operation is limited, such ions being generally restricted to those having atomic numbers 58–60, 62, and 64–71, the number of input signal frequencies capable of being amplified is also limited.

In accordance with the invention, it has been discovered that certain divalent metal-ion containing tungstate compositions ofm atter exhibit enhanced maser characteristics. when grown by the methods of the invention. The divalent metal-ion tungstates of the invention are calcium tungstate, strontium tungstate and barium tungstate, each having a noncubic crystalline lattice structure of the Scheelite type. From about 0.01 atom percent to 15 atom percent of the divalent ions are replaced by trivalent rare earth ions as the active maser material, the ions having atomic numbers 58–60, 62 and 64–71. Enhanced maser operation is dependent upon further incorporating in the crystal monovalent ions. The monovalent ions useful for enhancing maser operation are sodium, lithium and potassium.

In accordance with the method of the invention, a mixture of the desired divalent metal-ion tungstate or a divalent metal-ion compound that reacts with tungstic acid anhydride to form the tungstate, at least one trivalent rare-earth ion-containing substance having the desired rare-earth ions and at least one monovalent ion-containing substance having the desired monovalent ions, is heated to a temperature sufficient to form a molten solution. A seed crystal is inserted into the melt and slowly withdrawn therefrom, crystal growth being thereby promoted on the seed crystal.

It has been determined that the efficacy of the process is dependent upon the use of a critical amount of monovalent ion in the melt. In particular, the melt contains from 1.5 to 15 monovalent ions per trivalent ion in the melt with a maximum excess being attained when the melt contains 30 atom percent monovalent ion based on the number of divalent metal-ions present.

Tungstate crystals grown by the method of the invention are found to be particularly suitable for maser use and to possess enhanced maser characteristics. In particular, it is found that the distribution coefficient of the trivalent rare earth ions in the melt compared to the ions incorporated into the crystal is greatly improved. The use of the critical amount of excess monovalent ion in the melt results, for calcium tungstate crystals doped with neodymium, in the incorporation in the crystal of 0.83 atom percent neodymium when the melt contains one atom percent neodymium. As previously noted, the prior art technique results in the incorporation of only 0.24 atom percent neodymium from a melt con-

taining one atom percent of the ion. It has been found that the distribution coefficient of all trivalent ion materials of the invention is improved by the critical monovalent ion inclusions.

Further advantages accruing to crystals grown by the instant method may be more easily understood by reference to the drawing in which:

FIG. 1 on coordinates of relative emission intensity and wavelength in microns is a plot showing the fluorescent line spectrum of a calcium tungstate crystal grown from a melt containing 8 atom percent sodium and 8 atom percent neodymium, the resulting crystal containing 2 atom percent neodymium.

FIG. 2 on coordinates of relative emission intensity and wavelength in microns is a plot showing the fluorescent line spectrum of a calcium tungstate crystal grown from a melt containing 10 atom percent sodium and 2.5 atom percent neodymium, the resulting crystal containing 2 atom percent neodymium.

Referring more particularly to FIGS. 1 and 2, FIG. 1 depicts the fluorescent line spectrum of a tungstate crystal grown from a melt containing one monovalent ion per trivalent rare earth ion. Crystals grown from melts containing no monovalent ion or less than one monovalent ion per trivalent rare earth ion exhibit similar spectra. FIG. 2 depicts the spectrum of tungstate crystals grown from a melt containing four monovalent ions per trivalent rare earth ion. Crystals grown from melts containing 1.5 to 15 monovalent ions per trivalent rare earth ion exhibit similar spectra.

From a comparison of the figures, it is seen that critical inclusions in the melt result in a sodium shift of the primary fluorescent line from 1.066 microns, line **1**, to 1.065 microns, line **3**. This shift is illustrative of a further advantage accruing to the crystals of the invention; namely, by the critical monovalent ion additions to the melt, the primary emitting lines can be varied. The number of input signal frequencies capable of being amplified is accordingly increased by such monovalent ion inclusions.

Still another advantage accruing to the materials of the invention is an increase in intensity of the emitting lines. Such increase is illustrative by a comparison of the emission intensity of a second fluorescent line, line **4**, exhibited by the sodium-containing tungstate of this invention of FIG. 2, with a second fluorescent line, line **2**, of the usual sodium-containing tungstate of FIG. 1. Whereas the fluorescent line associated with the tungstate of the invention has a relative emission intensity of 60 percent of the most intense line, the equivalent fluorescent line associated with the tungstate of FIG. 1 has a relative emission intensity of only 50 percent of the most intense line. A comparison of the figures shows that such increase is due to minimization of other fluorescent lines by the incorporated sodium ions in the amount indicated.

A further advantage accruing to many materials of the invention is also illustrated by the preceding comparison of relative emission intensities. For the crystal of FIG. 2, a first fluorescent line, line 3, at approximately 1.064 microns, is observed under one joule of input power and a second fluorescent line, at approximately 1.065 microns, line 4, is observed under six joules of input power. In contrast, the crystal of FIG. 1 requires three joules of power for the first line, at approximately 1.065 microns, line 1, and eighteen joules of power for the next line, at approximately 1.066 microns, line 2. For many crystals of the invention, therefore, the minimum power, or threshold, required to produce emission is significantly lower than that required for conventional crystals grown by the prior art technique.

To obtain the lines of FIGS. 1 and 2, measurements were made with a Perkin Elmer grating spectrometer. Emission was excited by illuminating the sample with a mercury lamp and detecting the fluorescent light by means of a lead sulfide detector calibrated in arbitrary units of 0 to 1400.

The divalent metal ion tungstate may be introduced into the initial mixture as either the tungstate per se or as a compound such as a divalent metal-ion salt, oxide, nitrate or carbonate that will react with tungstic acid anhydride to form the tungstate. When a compound other than a tungstate is utilized, it is preferable that the by-products of the reaction volatize during the subsequent heating step. However, the only critical requirement is that such by-product does not act as a contaminant during growth of the tungstate crystal.

Typically, a stoichiometric amount of the divalent metal-ion compound and tungstic acid anhydride is utilized. However, deviations from the stoichiometry are permissible, such deviations being generally limited to an excess or deficiency of divalent metal ions in the order of 5 atom percent due to the tendency of second phase formation in the growing crystal for greater deviations.

The trivalent rare earth ions and monovalent ions may also be introduced into the initial mixture in the form of compounds such as oxides, carbonates, salts or nitrates that, under the processing conditions, form a melt with the tungstate.

As understood by the art, although in principle there is no lower limit on the concentration of trivalent rare-earth ion in the formed crystal, a practical limit of about 0.01 atom percent rare earth ion in place of the divalent metal ion of the tungstate host lattice is imposed by the necessity of having sufficient unpaired electrons available in the negative temperature state to adequately amplify the output signal. The preferred concentrations are in the order of 0.1 atom percent to four atom percent with maximum concentration being in the order of 15 atom percent. Concentrations above fifteen atom percent are considered undesirable due to difficulties encountered in forming strain-free crystals and line broadening effects associated with such concentrations which detract from the magnitude of amplification of the input signal.

Although not so limited, in accordance with a preferred embodiment herein, it is considered desirable to utilize an excess of twenty percent trivalent ion in the melt to compensate for the prior discussed distribution coefficient, thereby ensuring that the desired number of trivalent ions are incorporated into the grown crystal. A maximum trivalent ion concentration in the melt is therefore eighteen atom percent. In contrast, the distribution coefficient of the prior art technique dictates an excess of 317 percent trivalent ion in the melt.

The concentration of monovalent ions in the melt necessary to achieve the desired concentration in the crystal is critical. It has been determined that the melt must contain at least 1.5 monovalent ions per trivalent ion in order to produce the previously discussed improvements in tungstate crystals. It has been determined, for example, that the use of one monovalent ion per trivalent ion in the melt, results in crystals in which the distribution coefficient is not appreciably enhanced over monovalent ion-free crystals. Desirably, the melt contains monovalent ion additions up to 15 monovalent ions per trivalent ion. A maximum concentration in the melt of 30 atom percent results, however, due to difficulty in growing strain-free crystals. A preferred range of monovalent ion inclusions in the melt is from 3 to 10 monovalent ions per trivalent rare earth ion in the melt.

Monovalent alkali ions suitable for practicing the invention are sodium, lithium and potassium. The use of rubidium and cesium ions are precluded in the method because of their large ionic radii which introduces strain into the tungstate crystalline lattice.

There are no critical limits to particle sizes of the initial reactants since a molten solution is formed of the initial mixture. Generally, the non rare-earth ion impurity limit is not critical. Preferably the amount of accidentally

added trivalent rare-earth ion impurity should not exceed 0.1 the amount of the principal active trivalent rare-earth ion intentionally added. Ordinary reagent grade chemicals were used in the following specific examples and are suitable as the trivalent rare-earth ion impurity limits.

The above initial reactants are heated to a temperature sufficient to form a molten solution. This effect is readily determined visually. A typical initial mixture of calcium tungstate, 2.2 atom percent neodymium and 11 atom percent sodium requires a temperature of approximately 1550° C. to form a molten solution. In general, the mixtures of the invention melt at temperatures in the order of 1525° C. to 1625° C. To minimize contamination, a crucible made of an inert material such as rhodium or iridium is used to hold the initial mixture and the resulting melt during processing.

The atmosphere in which the heating is carried out is not critical. However, it is well known to use an inert or oxygen-containing atmosphere to prevent an ion in a higher valency state from being reduced to a lower valency state. For example, the tungsten ion, W^{+6}, is reduced to the lower valency state, W^{+5}, when a reducing atmosphere is used in conjunction with the elevated temperatures.

After sufficient heating to form a melt of the initial mixture, a seed crystal is inserted into the melt and slowly withdrawn therefrom. The composition of the seed crystal is not critical. The composition may range from undoped to heavily doped tungstate crystals. Although not necessary, the seed crystal is generally slowly rotated while being withdrawn from the melt when uniformity of crystal growth is desired on all surfaces of the seed crystal. A pulling rate of approximately one-half inch per hour and a rotation rate of 60 r.p.m. are convenient in the obtaining of large crystals. Other pulling rates are equally feasible, however, although it has been found that the growing crystal has a tendency to crack when rates substantially in excess of four inches per hour are utilized.

Specific examples of tungstate crystals grown by the method of the invention are given below. These examples are to be construed as illustrative only and not as limiting in any way the scope and spirit of the invention.

Example 1

100 grams $CaWO_4$, 1.3 grams Nd_2O_3, 2.7 grams WO_3 and 5.6 grams Na_2WO_4 were initially mixed together. The mixture was then heated in a rhodium crucible in air to a temperature of 150° C. to form a molten solution. The solution contained 4 sodium ions per neodymium ion. A seed crystal of calcium tungstate was then inserted into the melt and simultaneously rotated and withdrawn from the melt. The rotation rate was approximately 60 r.p.m. and the pulling rate was approximately one-half inch per hour. The resulting calcium tungstate crystal contained approximately two atom percent neodymium.

Example 2

100 grams $CaWO_4$, 0.2 gram $Ce_2(WO_4)_3$ and 0.55 gram Li_2WO_4 were initially mixed together. The mixture was then heated in an iridium crucible in air to a temperature of 1600° C. to form a molten solution. The solution contained 10 lithium ions per cerium ion. A seed crystal of calcium tungstate was then inserted into the melt and simultaneously rotated at 100 r.p.m. and withdrawn from the melt at two inches per hour. The resulting calcium tungstate crystal contained approximately 0.1 atom percent cerium.

Example 3

100 grams $SrWO_4$, 2.1 grams $NaTm(WO_4)_2$ and 3.6 grams Na_2WO_4 were initially mixed together. The mixture was then heated in a rhodium crucible in air to a temperature of 1580° C. to form a molten solution. The solution contained 5 sodium ions per thulium ion. A seed crystal of strontium tungstate was then inserted into the melt and withdrawn therefrom at one-half inch per hour. The resulting strontium tungstate crystal contained approximately one atom percent thulium.

What is claimed is:

1. A process for growing single crystals of calcium tungstate comprising forming a mixture of initial ingredients equivalent to $CaWO_4$ together with a trivalent neodymium ion-containing substance containing from about 0.01 atom percent to 18 atom percent based on the total calcium ions present of neodymium ion and a monovalent sodium ion-containing substance containing from about 1.5 sodium ions to 15 sodium ions per neodymium ion present, up to a maximum of 30 atom percent based on the total calcium ions present, heating said initial ingredients to a temperature sufficient to form a molten solution, inserting a seed crystal into said molten solution and slowly withdrawing said seed crystal from said solution, thereby promoting crystal growth on said seed crystal.

2. A process in accordance with claim **1** wherein said neodymium-containing substance contains from about 0.1 to 4.0 atom percent of neodymium.

3. A process in accordance with claim **2** wherein the said sodium-containing substances contains from about 3 to 10 sodium ions per neodymium ion.

References Cited by the Examiner

UNITED STATES PATENTS

2,954,300	9/1960	Triebwasser.	
3,003,112	10/1961	Van Uitert	23—301 X
3,053,635	9/1962	Shockley	23—301 X

OTHER REFERENCES

Kroger: Some Aspects of the Luminescence of Solids, Elsevier Pub. Co., New York, 1948, pages 290–298.

Nassau et al.: "Preparation of Large Calcium-Tungstate Crystals Containing Paramagnetic Ions for Maser Applications," J. App. Phys., vol. 31, #8, August 1960, page 1508.

TOBIAS E. LEVOW, *Primary Examiner.*
MAURICE A. BRINDISI, *Examiner.*
R. D. EDMONDS, *Assistant Examiner.*