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NIOBATE MASER MATERIALS AND DEVICES MADE THEREFROM

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FIG. 1

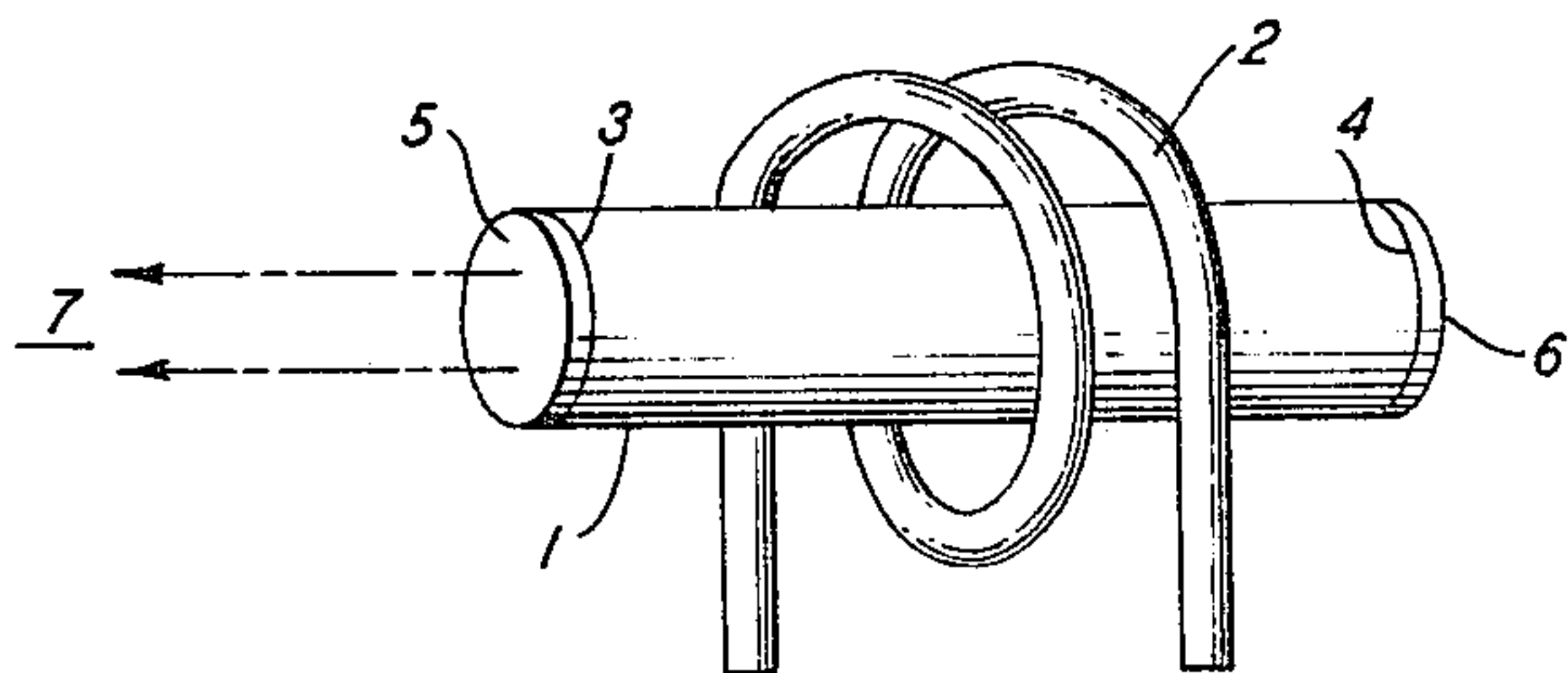
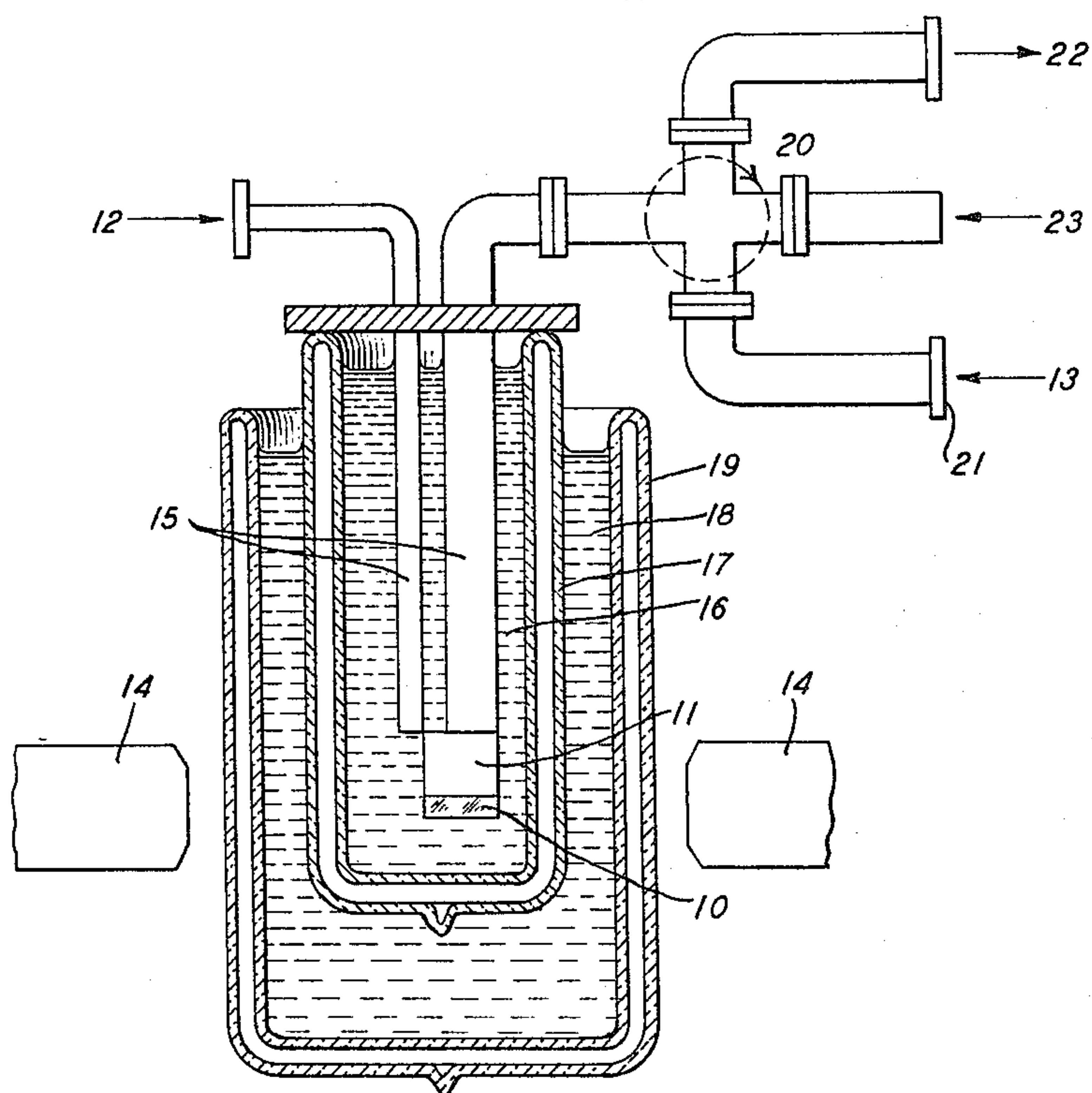


FIG. 2



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1

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NIOBATE MASER MATERIALS AND DEVICES MADE THEREFROM

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This invention relates to single crystal niobate materials and to devices utilizing such materials.

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 "The Maser," pages 86 to 94 of the August 1962 issue of the Microwave Journal. 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. Such devices and the mechanics of their operation are described in detail in, for example, the article entitled, "Lasers: Devices and Systems—Part I," pages 38 to 47, of the October 27, 1961, issue of Electronics, and the article entitled, "Infrared and Optical Masers," pages 21 to 29, of the June 1961 issue of The Solid State Journal.

As discussed in these articles, the heart of the solid state maser is a crystal lattice to which an impurity has been added. The impurity is a material containing ions with more than one unpaired electron, and it is these ions which provide the maser action. The crystal itself merely acts as a host in which the energy oscillations can take place. The mechanics of establishing the requisite nonequilibrium electron population distribution in a pair of energy levels of the ions, termed a negative temperature state, and subsequently amplifying a signal of a frequency which satisfies Planck's law with respect to the two energy levels in nonequilibrium is described in detail in these articles.

The articles further note that the number of materials suitable for maser operation is limited, with the development of new materials being necessary if masers are to operate over a wide range of wavelengths. The list of active ions considered advantageous to stimulate the emission of radiation is, by now, quite long and includes the rare earth ions, particularly those having atomic numbers 59, 60, 62 to 70, and 92 and the transition metal ions nickel, manganese, cobalt, copper, iron and chromium. The number of host lattices capable of accepting these ions is limited however.

In accordance with the invention, it has been discovered that certain divalent metal ion niobate compositions of matter accept and provide enhanced lattice environments for the rare earth and transition metal ions which provide maser action. The divalent metal ions of the invention are calcium, magnesium, strontium, manganese, and zinc.

It has been further discovered that niobate host lattices including two or more of the above divalent metal ions are permissible and result in additional suitable host lattices for the active ions. In particular, such permissible plural incorporations are as follows:

ANb_2O_6 , where A is at least one divalent ion selected from the group consisting of calcium and manganese;

BNb_2O_6 , where B is at least one divalent ion selected from the group consisting of magnesium, zinc, and manganese; and

2

CNb_2O_6 , where C is at least one divalent ion selected from the group consisting of calcium and strontium.

It has been found that the lattice defined as CNb_2O_6 also accepts divalent barium ions in limited amounts, the resulting lattice thereby providing an additional environment for the active ions. In particular, lattices in which up to 40 atomic percent of the divalent C ions have been replaced by barium ions are permissible.

Commensurate with the art and the preceding discussion, maser materials result when restricted amounts of the divalent ions of the host lattice are replaced by rare earth ions and transition metal ions. Particularly suitable rare earth ions are those in the +3 valency state having atomic numbers 60, 67, 68, 70, 92 and those in either the +2 or +3 valency state having atomic numbers 59, 62 to 66, 69. Suitable transition ions are manganese, nickel, cobalt and copper in the +2 valency state, chromium in the +3 valency state, and iron in either the +2 or +3 valency state.

The host lattices of the invention may optionally include restricted amounts of monovalent alkali metal ions and tetravalent titanium and zirconium ions which compensate for the charge of the trivalent active ions incorporated in the host lattice. The monovalent alkali ions include sodium, lithium, rubidium, potassium, and cesium.

The materials of the invention emit energy of narrow line width. Neodymium-containing calcium niobate crystals, for example, emit radiation at room temperature having a wavelength of approximately 1.06 microns. The line width associated with this fluorescence is approximately 2.5 cm^{-1} . In contrast, the line width associated with the same wavelength for comparable neodymium-containing calcium tungstate crystals is in the order of 6 cm^{-1} .

The excited electrons of the ions incorporated in the host lattices of the invention evidence lifetimes sufficiently long so that the quantum efficiency for masing is close to unity. Illustrative of such lifetimes is the 2.2 millisecond lifetime associated holmium-containing calcium niobate crystals at liquid nitrogen temperature.

A further advantage accruing to the materials of the invention is the transparency of the host lattices to radiation over a broad wavelength range. The calcium niobate lattice, for example, is transparent to radiation over the range of from 0.3 micron to 5.5 microns. In contrast, calcium tungstate lattices are transparent over the more restricted range of from 0.3 micron to 4 microns.

The invention may be more easily understood by reference to the drawing, in which:

FIG. 1 is a perspective view of an optical maser device utilizing compositions of the invention; and

FIG. 2 is a sectional view of a microwave maser device utilizing compositions of the invention.

Referring more particularly to FIG. 1, there is shown a rod-shaped crystal 1 having the composition as disclosed herein. Pump energy is supplied by means of a helical lamp 2 encompassing rod 1 and connected to an energy source not shown. Lamp 2 is advantageously of a type which produces intense radiation over a broad band typically extending from about 0.2 micron to 2.5 microns. Xenon lamps, for example, are considered useful to pump the material of the invention. Ends 3 and 4 of rod 1 are ground and polished so as to be optically flat and parallel and are silvered so as to provide reflective layers 5 and 6. As indicated, layer 6 is completely reflecting, while layer 5 is only partially reflecting, so permitting the escape of coherent radiation 7. Rod 1 during operation is typically maintained at liquid nitrogen temperature so as to more readily obtain a negative temperature state. An exception is neodymium-containing calcium niobate crystals which are readily operable at room temperature.

Optical masers of the general type illustrated in the figure have been operated using as the active maser material the host lattices of the invention containing the recognized fluorescent impurity ions of the art. These ions include those previously detailed herein with the exception of iron, whose primary utility is considered to be in microwave applications. Illustrative examples of such maser operation are given below.

Example 1

An optical maser was operated using as the active medium calcium niobate containing about 0.5 atomic percent neodymium in place of calcium. The device produced intense coherent emission with a xenon pump having a wavelength of about 1.06 microns at room temperature. The threshold power required was two joules.

Example 2

An optical maser was operated using as the active medium calcium niobate containing about 0.5 atomic percent praseodymium in place of calcium. The device produced intense coherent emission with a xenon pump having a wavelength of about 1.04 microns at liquid nitrogen temperature. The threshold power required was 25 joules. A strong visible red emission also occurred under these conditions.

Example 3

An optical maser was operated using as the active medium calcium niobate containing about 0.5 atomic percent holmium in place of calcium. The device produced intense coherent emission with a xenon pump having a wavelength of about 2.04 microns at liquid nitrogen temperature. The threshold power required was 90 joules. A strong visible green emission also occurred under these conditions.

In FIG. 2 there is shown an illustrative microwave maser device in which amplification of an input signal takes place by stimulated emission of radiation from crystals of the invention. The device is described in detail in the 1958 November/December issue of the Microwave Journal, pages 19 and 20. Briefly, a crystal 10 of the invention is located in cavity 11 designed to support microwave energy at two different frequencies, one being the pump frequency 12 and the other being the signal frequency 13. The crystal is acted upon by a D.C. magnetic field produced by pole pieces 14 and by two RF magnetic fields associated with the two frequencies 12 and 13 produced by means not shown. The cavity 11 and associated waveguides 15 which couple the two RF energies into the cavity tube are immersed in a liquid helium bath 16 which is contained in a Dewar flask 17. Flask 17, in turn, is immersed in a liquid nitrogen bath 18 which is contained in a Dewar flask 19. The circulator 20 is a four-terminal pair device with a nonreciprocal property indicated by its symbol. A signal from antenna 21 is sent to cavity 11. The amplified signal from cavity 11 is sent to receiver 22. Any reflected signal from the receiver 22 is directed to a dummy load 23, where it is adsorbed.

Of the ions previously detailed herein, the noted transition metal ions and gadolinium in the +2 and +3 valency states are considered particularly suitable for use as the active maser material.

It is noted that device discussion has been largely in terms of the most commonly reported maser design. Although such a design is easily fabricated, other configurations have been disclosed in the literature and are considered within the scope of the invention.

As understood by the art, although in principle there is no lower limit on the concentration of active ions utilized, a practical limit of about 0.01 atom percent active ion in place of the divalent metal ions of the host lattice is imposed by the necessity of creating a sufficient electron population inversion to provide adequate maser action. The optimum concentrations for minimum thresholds and line widths and maximum lifetimes are of the

order of from 0.1 to 2.0 atom percent for the materials of the invention. Increasing concentrations above this level to a maximum of about 10 atom percent are permissible, however, with accompanying line broadening, increased thresholds, and decreased lifetimes.

It has been determined that the incorporation of more than one type of active ion in the lattices of the invention is permissible as concerns crystal growth and maser action.

The niobate compositions of the invention are conveniently made by a method generally described as the Czochralski method. This method is described in an article by J. Czochralski in Zeitschrift fur Physikalische Chemie, volume 92, pages 219 to 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 components, the composition of the melt being the desired composition of the grown crystal. A seed crystal is inserted into the melt and simultaneously rotated and slowly withdrawn therefrom. Charge compensation occurs in the lattice of the crystal by the substitution of two trivalent active ions for three divalent ions of the lattice or one divalent active ion for one divalent ion of the lattice.

A variety of compositions of the invention have been grown by the Czochralski melt technique. Specific examples of the procedures utilized in the preparation of several such compositions are given below.

Example 4

40 grams of CaCO_3 , 106 grams of Nb_2O_5 , and 0.84 gram of Nd_2O_3 were melted in an iridium crucible. A seed crystal was inserted into the top surface of the melt and was simultaneously rotated and drawn from the melt. The speed of rotation was about 30 r.p.m. and the rate of drawing was about one-fifth inch per hour. The resulting calcium niobate crystal contained about 0.3 percent trivalent neodymium in place of calcium.

Example 5

34 grams of MgCO_3 , 106 grams of Nb_2O_5 , and 0.84 gram of Eu_2O_3 were melted and processed in accordance with the procedure of Example 4. The resulting magnesium niobate crystal contained about 0.3 percent trivalent europium in place of magnesium.

Example 6

59 grams of SrCO_3 , 106 grams of Nb_2O_5 , and 0.27 gram of UO_2 were melted and processed in accordance with the procedure of Example 4. The resulting strontium niobate crystal contained about 0.2 percent trivalent uranium in place of strontium.

Example 7

46 grams of MnCO_3 , 106 grams of Nb_2O_5 , and 1 gram of CrO_3 were melted and processed in accordance with the procedure of Example 4. The resulting manganese niobate crystal contained about 0.5 percent trivalent chromium in place of manganese.

Example 8

32 grams of ZnO , 106 grams of Nb_2O_5 , and 0.75 gram of Fe_2O_3 were melted and processed in accordance with the procedure of Example 4. The resulting zinc niobate crystal contained about 0.3 percent trivalent iron in place of zinc.

Example 9

The crystal resulting in Example 8 was bombarded with gamma rays from a cobalt source for a period of 12 hours. The trivalent iron ions in the crystal were reduced to the 2+ valency state.

Example 10

20 grams of CaCO_3 , 23 grams of MnCO_3 , 106 grams of Nb_2O_5 , and 0.75 gram of NiO were melted and proc-

5

essed in accordance with the procedure of Example 4. The resulting calcium-manganese niobate crystal contained 1.0 percent divalent nickel in place of the calcium and manganese ions.

Example 11

8.5 grams of $MgCO_3$, 11.5 grams of $MnCO_3$, 8.0 grams of ZnO , 106 grams of Nb_2O_5 , and 0.35 gram of Sm_2O_3 were melted and processed in accordance with the procedure of Example 4. The resulting magnesium-manganese-zinc niobate crystal contained 0.3 percent trivalent samarium in place of magnesium, manganese and zinc.

Example 12

The crystal resulting in Example 11 was processed in accordance with the procedure of Example 9 with the resulting reduction of trivalent samarium to divalent samarium.

Example 13

10 grams of $CaCO_3$, 14.7 grams of $SrCO_3$, 53 grams of Nb_2O_5 , and 0.75 grams of CoO were melted and processed in accordance with the procedure of Example 4. The resulting calcium-strontium niobate crystal contained 1.0 percent divalent cobalt in place of the calcium and strontium ions.

As discussed previously, it has been determined that charge compensation in the crystals of the invention is permissible by the further incorporation in the host lattices of monovalent alkali ions and tetravalent titanium and zirconium ions. Such incorporation necessitates the addition to the Czochralski melt of substances containing these ions, for example oxides, salts, and the like. Preferably, by-products of these substances volatilize during heating, but it is only necessary that such by-products do not act as contaminants during crystal growth. Partial or complete charge compensation is preferably achieved by incorporating up to two atom percent of the compensating ions. One monovalent compensating ion and one trivalent active ion substitute for two divalent host lattice ions and one tetravalent compensating ion and one trivalent doping ion substitute for one niobium +5 ion and one divalent host lattice ion, respectively. Charge compensation is achieved with compensating ion substitutions up to ten atom percent, although a tendency for second phase formation may be encountered.

Illustrative examples of procedures utilized in the preparation of charge compensated crystals of the invention are given below.

Example 14

40 grams of $CaCO_3$, 108.7 grams of Nb_2O_5 , 0.84 gram of Nd_2O_3 , and 0.26 gram of Na_2CO_3 were melted and processed in accordance with the procedure of Example 4. The resulting calcium niobate crystal contained about 0.5 percent neodymium and 0.7 percent sodium in place of calcium.

Example 15

59 grams of $SrCO_3$, 107.6 grams of Nb_2O_5 , 0.84 gram of Nd_2O_3 , and 0.32 gram of TiO_2 were melted and processed in accordance with the procedure of Example 4. The resulting strontium niobate crystal contained 0.5 percent neodymium in place of strontium and 0.7 percent titanium in place of niobium.

6

Although the invention has been described with reference to specific embodiments, these embodiments are to be construed as illustrative only and not as limiting the scope and spirit of the invention as defined by the appended claims.

What is claimed is:

1. A crystalline composition of matter having the empirical formula



where A is at least one divalent host ion selected from the group consisting of calcium, magnesium, zinc and strontium and in which from about 0.01 percent to 10 percent of the divalent host ions have been replaced by at least one active ion selected from the group consisting of rare earth ions in the +3 valency state having atomic numbers 59, 60, 62-70, 92; rare earth ions in the +2 valency state having atomic numbers 59, 62-66, 69; Fe, Mn, Ni, Co, Cu transition metal ions in the +2 valency state; and Fe, Cu transition metal ions in the +3 valency state and in which up to 40 percent of said calcium and strontium ions have been replaced by barium ions.

2. A composition of matter in accordance with claim 1 wherein from about 0.1 percent to 2 percent of said divalent host ions have been replaced by at least one of said active ions.

3. An optical maser comprising means forming an optical cavity resonator, a negative temperature medium disposed within said resonator, said medium consisting essentially of a crystalline composition having the empirical formula



where A is at least one divalent host ion selected from the group consisting of calcium, magnesium, zinc and strontium and in which from about 0.01 percent to 10 percent of the divalent host ions have been replaced by at least one active ion selected from the group consisting of rare earth ions in the +3 valency state having atomic numbers 59, 60, 62-70, 92; rare earth ions in the +2 valency state having atomic numbers 59, 62-66, 69; Fe, Mn, Ni, Co, Cu transition metal ions in the +2 valency state; and Fe, Cu transition metal ions in the +3 valency state and in which up to 40 percent of said calcium and strontium ions have been replaced by barium ions, and means for pumping said medium to produce a population inversion between a pair of optically connected energy levels of said negative temperature medium.

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