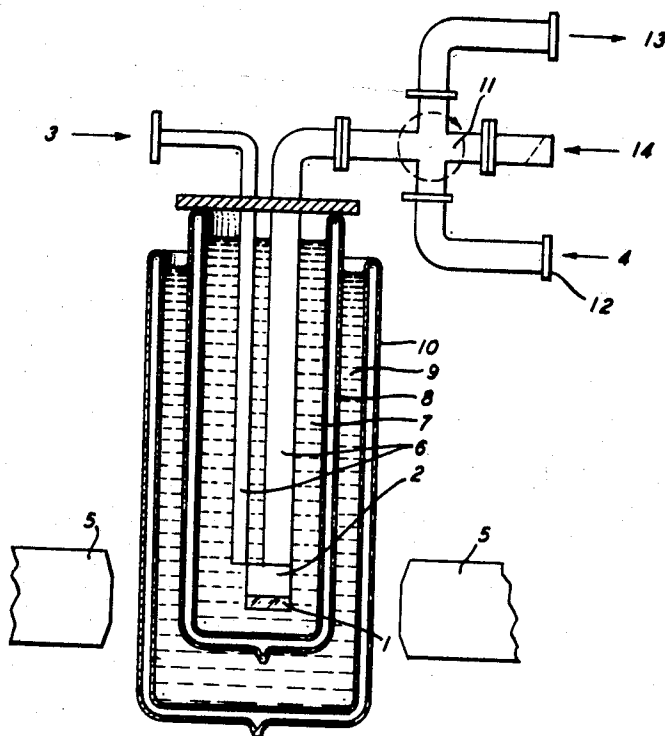


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INDIUM TUNGSTATE
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MICROWAVE MASER MATERIALS CONSISTING OF CHROMIUM DOPED SODIUM INDIUM TUNGSTATE AND IRON DOPED SODIUM INDIUM TUNGSTATE

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This invention relates to single crystal tungstate materials containing small additions of paramagnetic ions and to devices utilizing such crystals.

In recent years a new amplification principle, that of microwave amplification by stimulated emission of radiation, has been developed. The mechanics of this principle, and devices known as masers utilizing it, 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 of Electronics, Engineering Edition, April 25, 1958.

Among the more promising microwave maser materials are those which include a diamagnetic host crystal containing small amounts of paramagnetic ion from which the stimulated emission occurs. Due to the influence of the internal electrical field of the host crystal, the materials are characterized by a large zero field splitting of the unpaired electrons of the paramagnetic ion, resulting in at least three energy levels. The mechanics of establishing the requisite nonequilibrium electron population distribution in a pair of the energy levels and subsequently amplifying a signal of a frequency which satisfies Planck's Law with respect to the two energy levels in nonequilibrium is understood by the art.

Among the more successful paramagnetic ions used to stimulate emission are iron and chromium ions in the 3+ valency state. In accordance with the preceding discussion, these ions are characterized by zero field splittings, the magnitude of which is dependent upon the host lattice in which they are incorporated. Since there is a correspondence between the signal to be amplified and zero field splitting, the range of signal frequencies amplified by these ions is dependent upon the range of zero field splittings exhibited by the ions. Unfortunately, the range of splittings is limited due to the relatively few host lattices capable of accepting the ions. Such lattices include, for example, rutile, aluminum oxide and beryl.

In accordance with the invention, a new host lattice capable of accepting trivalent chromium and iron ions has been discovered. The large zero field splittings evidenced by the ions in this lattice are conducive to the amplification of large signal frequencies. More particularly, it has been found that a monovalent-trivalent metal ion tungstate of the composition $\text{Na}_{0.5}\text{In}_{0.5}\text{WO}_4$, in which restricted amounts of the trivalent indium ions have been replaced by chromium, iron, or chromium and iron in the 3+ valency state, is useful for amplifying microwave signals. The subscripts in the above formula signify the relative number of gram atoms of the elements indicated which are present and thus are also proportional to the relative number of atoms of each element present in the composition.

In the following table there is tabulated the approximate zero field splittings of the unpaired electrons of the chromium and iron ions in the host lattice of the invention. For comparison, the zero field splittings of these ions in illustrative prior art host lattices are also given. In accordance with the conventions of the maser art, the zero field splittings are expressed in terms of frequency for convenience.

TABLE 1

Host Lattice	Zero Field Splitting in kmc.	
	Chromium	Iron
Sodium-indium tungstate.....	66.8	61.2
Rutile.....	43	43
Aluminum oxide.....	11.5	11
Beryl.....	53.6	6

The large zero field splittings realized by the chromium and iron ions in the host lattice of the invention are conducive to the amplifying of signal frequencies up to approximately 75 kmc. Signal amplification up to approximately 61 kmc. is associated with the 53.6 kmc. zero field splitting of emerald. The progressively smaller splittings associated with the rutile and aluminum oxide lattices cause a corresponding decrease in emission frequency.

The invention may be more easily understood by reference to the drawing in which the figure is a sectional view of an apparatus utilizing the composition of the invention.

Referring more particularly to the figure, there is shown an illustrative microwave maser device in which amplification of an input signal takes place by stimulated emission of radiation from the tungstate crystals of the invention. This device is described in detail in the 1958 November/December issue of The Microwave Journal, pages 19 and 20. Briefly, a crystal 1 of the invention is located in cavity 2, designed to support microwave energy at two different frequencies, one being the pump frequency 3 and the other being the signal frequency 4. The crystal is acted upon by a direct-current magnetic field produced by pole pieces 5 and by two RF magnetic fields associated with the two frequencies 3 and 4 produced by means not shown. The cavity 2 and associated waveguides 6, which couple the two RF energies into the cavity tube, are immersed in a liquid helium bath 7 which is contained in a Dewar flask 8. Flask 8, in turn, is immersed in a liquid nitrogen bath 9 which is contained in a Dewar flask 10. The circulator 11 is a four-terminal pair device with a nonreciprocal property indicated by its symbol. A signal from antenna 12 is sent to cavity 2. The amplified signal from cavity 2 is sent to receiver 13. Any reflected signal from the receiver 13 is directed to a dummy load 14, where it is absorbed.

In one illustrative embodiment, a D-C. magnetic field of 10,000 gauss and an RF pumping frequency of 95 kmc. is utilized in conjunction with a chromium-doped sodium-indium tungstate crystal of the invention to amplify a 50 kmc. signal.

As understood by the art, although in principle there is no lower limit on the concentration of the chromium or iron ions utilized, a practical limit of about 0.01 atom percent iron or chromium in place of the trivalent indium ion of the host lattice is imposed by the necessity of having sufficient unpaired electrons available in the negative temperature state to adequately amplify the input signal. The optimum concentrations for maximum amplification in general are of the order of from 0.05 to 0.5 percent for the materials of the invention. Amplification is obtained with higher concentrations above this level to a maximum of about 5 percent. However, the accompanying line broadening effects detract from the magnitude of amplification of the input signal. Such increased concentrations are useful for devices requiring a substantially increased band width.

It has been further determined that both chromium and iron in the 3+ valency state can be incorporated in the sodium-indium tungstate host lattice with a resulting improvement in maser operation. In such double incor-

poration, chromium is the principal active paramagnetic ion, with iron being employed to shorten the recovery time of the chromium electrons. As is understood by the art, it is advantageous to have the relaxation time of electron transitions from the lowest level of the nonequilibrium pair of spaced energy levels to the bottom level of the selected three-level energy system as short as possible. A short recovery time permits more electrons to become available for pumping to the upper level of the nonequilibrium pair of spaced energy levels, thereby maximizing the efficiency of maser action. As is further understood by the art, such relaxation can be shortened by incorporating in the host lattice a second paramagnetic ion. This second, or nonamplifying, ion is chosen such that, due to a mechanism of energy exchange with the principal active paramagnetic ion, the recovery time of the principal active ion is shortened. The mechanisms of this effect are described in detail in Patent No. 2,981,894, issued April 25, 1961.

When trivalent iron is utilized in combination with trivalent chromium in this fashion, a practical minimum limit of about 0.1 atom percent iron in place of the trivalent indium ion of the host lattice is imposed by the necessity of having a sufficient concentration of iron ions available for interaction with the chromium ions. An optimum iron concentration is in the order of one to five percent. Enhancement of the recovery time of the chromium electrons increases with increasing concentration of iron ions above this level to a maximum of about 10 atom percent. Beyond this limit, interactions between the chromium and the iron ions result in a significant increase in chromium line broadening.

The tungstate compositions of the invention are conveniently made by conventional methods known to the art. Such methods include the flux method disclosed in United States Patent 3,003,142, issued November 3, 1961 and the Czochralski method described in an article by J. Czochralski in *Zeitschrift für Physikalische Chemie*, volume 92, pages 219 to 221 (1918).

A recent description of the Czochralski method 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 top surface of the melt and simultaneously rotated and slowly withdrawn from the melt.

In accordance with the flux method, a flux of sodium tungstate is utilized to promote crystal growth, the sodium ions being incorporated into the crystalline lattice during such growth. Specific examples of compositions grown by this method are given below. These examples are to be construed as illustrative only and not as limiting in any manner the scope and spirit of the invention.

Example 1

255.7 grams Na_2WO_4 , 214.52 grams WO_3 , 20.8 grams In_2O_3 , and 0.0228 gram Cr_2O_3 were dry mixed together. The mixture was then heated in a platinum crucible in air for 16 hours at temperature of 1120°C . The molten solution so formed was then cooled in air at a controlled rate of 2.5°C . per hour to a temperature of 700°C . The resulting solids were then furnace cooled to room temperature and washed with hot sodium hydroxide, leaving sodium-indium tungstate crystals doped with trivalent chromium. The formed sodium-indium tungstate crystals contained about 0.1 percent chromium in place of indium.

Example 2

255.7 grams Na_2WO_4 , 214.52 grams WO_3 , 20.8 grams In_2O_3 , and 0.0239 gram Fe_2O_3 were dry mixed. The mixture then underwent the same processing as detailed above, with the resulting formation of sodium-indium tungstate crystals doped with trivalent iron. The formed sodium-indium tungstate crystals contained about 0.1 percent iron in place of indium.

Example 3

255.7 grams Na_2WO_4 , 214.52 grams WO_3 , 20.8 grams In_2O_3 , 0.0228 gram Cr_2O_3 , and 0.12 gram Fe_2O_3 were dry mixed. The mixture then underwent the same processing as detailed above, with the resulting formation of sodium-indium tungstate crystals doped with trivalent iron and trivalent chromium. The formed sodium-indium tungstate crystals contained about 0.1 percent chromium and 0.5 percent iron in place of indium.

What is claimed is:

1. A composition of matter consisting essentially of a single crystal sodium-indium tungstate material of the composition $\text{Na}_{0.5}\text{In}_{0.5}\text{WO}_4$ in which from about 0.01 to 5 percent of the trivalent indium ions have been replaced by at least one trivalent ion selected from the group consisting of chromium and iron, but where both iron and chromium are incorporated into the material, from about 0.1 to 10 percent of the indium ions are replaced by iron ions and from about 0.01 to 5 percent of the indium ions are replaced by chromium ions.

2. A composition of matter in accordance with claim 1 in which from about 0.05 to 0.5 percent of the trivalent indium ions have been replaced by at least one trivalent ion selected from the group consisting of chromium and iron, but where both iron and chromium are incorporated into the material, from about 1 to 5 percent of the indium ions are replaced by iron ions and from about 0.05 to 0.5 percent of the indium ions are replaced by chromium ions.

References Cited in the file of this patent

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3,003,112	Van Uitert	Oct. 3, 1961
3,015,072	Schulz-Du Bois et al.	Dec. 26, 1961