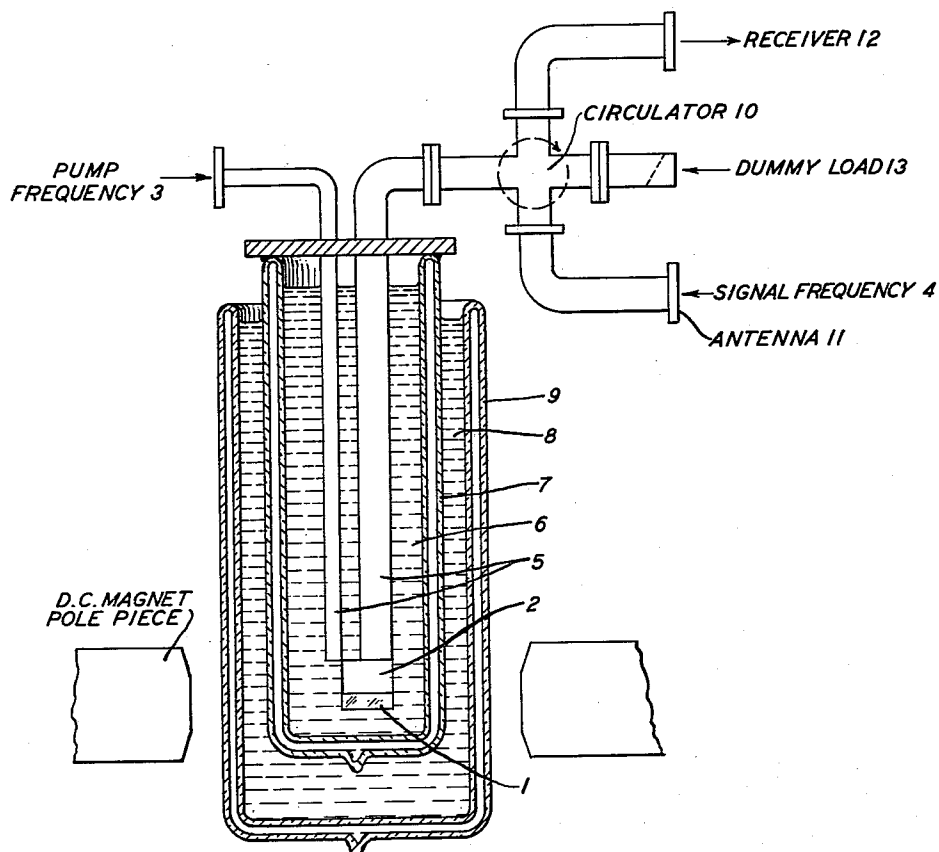


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LE GRAND G. VAN UITERT
PROCESS FOR GROWING AND APPARATUS FOR
UTILIZING PARAMAGNETIC CRYSTALS
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PROCESS FOR GROWING AND APPARATUS FOR UTILIZING PARAMAGNETIC CRYSTALS**Le Grand G. Van Uitert, Morris Township, Morris County, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York****Filed May 25, 1959, Ser. No. 815,542
10 Claims. (Cl. 330-4)**

This invention relates to a method of growing single crystal tungstates containing small additions of paramagnetic ions, to crystals so grown 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 phenomenon and devices known as masers utilizing it are well detailed in the literature as, for example, in the article entitled "The Maser," page 18 of The Microwave Journal for November/December 1958, and the article entitled "The Solid-State Maser—A Supercooled Amplifier," page 16 of "Electronics," Engineering Edition, April 25, 1958. Solid state maser devices in use today make use of a diamagnetic host crystal containing small amounts of a paramagnetic substance. The general properties that the host crystal and paramagnetic substance should exhibit for satisfactory maser action are outlined in the above-mentioned maser article in the November/December issue of The Microwave Journal. As evidenced by this article, very few maser materials are known to the art. Most published work on masers is directed to ruby and potassium cobalt cyanide crystals doped with chromium.

It is recognized that there should be a correspondence between the signal to be amplified and the zero field energy separations of the maser material. Therefore it is desirable that new maser materials having a range of zero field separations be developed so that a range of signals can be amplified.

Briefly, in accordance with the present invention, a divalent metal ion tungstate host crystal of the composition MWO_4 containing at least one paramagnetic ion selected from the group of such ions having atomic numbers 22 through 29 and 58 through 71 is useful in maser devices. M is a divalent metal ion such as calcium, magnesium, zinc, cadmium, strontium and barium. These crystals are grown by the methods of the present invention.

In accordance with the methods of this invention, a mixture of a divalent metal ion tungstate or a divalent metal ion compound that will react to form the tungstate and at least one paramagnetic ion-containing substance having one of the desired paramagnetic ions is heated in an alkali metal ditungstate flux, for example, sodium ditungstate, to a temperature sufficient to form a molten solution. The flux which is a solvent for the divalent metal ion tungstate may contain an excess of tungstic anhydride to enhance the solubility of the initial components. Rather than initially using an alkali metal ditungstate flux per se, compounds that will react to form the alkali metal ditungstate may be used.

The molten solution is then cooled at a controlled rate until it solidifies forming divalent metal ion tungstate crystals and the alkali metal ditungstate, which latter is removed thereby leaving the tungstate crystals.

The resulting diamagnetic tungstate crystals containing a small amount of a paramagnetic ion possess characteristics suitable for maser use. For example, the crystals exhibit a large zero field splitting and negligible hyperfine interaction. They are homogeneous and chemically stable. The paramagnetic ions are located in equivalent

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sites in the crystal thereby contributing to relatively narrow line widths. The unpaired electrons exhibit sufficiently long relaxation times to be useful. These characteristics are evidenced by various measurements tabulated in the following table made on representative crystals grown by the methods of this invention. In accordance with the conventions of the maser art, zero field splittings are expressed in terms of frequency for convenience. The measurements were made at temperatures approximating those actually used in maser operation. This was done since zero field splittings are temperature dependent in that a significant difference is observed in the splittings at temperatures approaching absolute zero as compared to room temperature. There is little difference, however, in splittings at temperatures between zero degree Kelvin and 100° Kelvin. Paramagnetic resonance measurements indicate that the spin lattice relaxation time at 77° Kelvin for these crystals is longer than 10^{-7} seconds.

TABLE I

Host Tungstate Crystal	Para-Magnetic Ion	Temperature, ° K.	Zero Field Splitting, Kilomegacycles	Line Width Megacycles
Calcium.....	Gadolinium.....	77	5.5; 10; 16.5	6.7
Strontium.....	do.....	77	5.4; 8.7; 15	28
Cadmium.....	Trivalent iron.....	77	56.8; 91.1	100
Magnesium.....	Trivalent chromium.....	77	48	100
Do.....	Trivalent iron.....	2 and 77	61.6; 75.6	200

In the accompanying figure, there is shown an illustrative microwave device in which amplification of an input signal takes place by the stimulated emission of radiation from crystals grown by the methods of the present invention. This device is described in detail in the 1958 November/December issue of The Microwave Journal, pages 19 and 20. Briefly, a paramagnetic crystal 1 grown by the methods of the instant invention is located in a 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 and by the two RF magnetic fields associated with the two frequencies. The cavity 2 and associated waveguides 5 which couple the two RF energies into the cavity 2 are immersed in a liquid helium bath 6 which is contained in a Dewar flask 7. Flask 7 in turn is immersed in a liquid nitrogen bath 8 which is contained in Dewar flask 9. The circulator 10 is a four-terminal pair device with a nonreciprocal property indicated by its symbol. A signal from antenna 11 is sent to the cavity 2. The amplified signal from cavity 2 is sent to the receiver 12. Any reflected signal from receiver 12 is directed to a dummy load 13 where it is absorbed.

In the following table there are tabulated illustrative embodiments using maser crystals of the instant invention together with appropriate values for the direct current magnetic field, RF pumping frequency and the input signal.

TABLE II

Host Tungstate Crystal	Para-Magnetic Ion	D.C. Magnetic Field, Gauss	RF Pumping Frequency, Kilomegacycles	Signal, Kilomegacycles
Calcium.....	Gadolinium.....	8,000	55	23
Cadmium.....	Trivalent iron.....	3,000	148	57
Magnesium.....	Trivalent chromium.....	4,000	60	40
Do.....	Trivalent iron.....	500	137	62
Strontium.....	Gadolinium.....	8,000	55	23

The divalent metal ion of the host material 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 tungstate anhydride to form the divalent metal ion tungstate. When the divalent metal ion is in the form of a compound other than a tungstate, it is preferable that by-products of the reaction volatilize during the following heating step. However, the only critical requirement is that such by-product does not act as a contaminant during growth of the tungstate crystal.

The paramagnetic ion or ions may be introduced into the initial mixture in the form of compounds such as oxides, carbonates, salts or nitrates that under the processing conditions will be soluble in the flux. Again, it is preferable that by-products of the reaction volatilize during heating but it is only necessary that such by-product not act as a contaminate during growth of the tungstate crystal.

As is known, it may be advantageous to use two or more different paramagnetic ions with different spin relaxation times to improve maser recovery. In such a case, the maser material would exhibit long pump and signal relaxation times and a short idler relaxation time. For example, in a three-level maser in which amplification occurs from the third to the second level, the spin relaxation times from level three to level two and level three to level one would be long. The relaxation time from level two to level one would be short. For a more detailed description of this effect, reference is made to patent application Serial No. 625,548, filed November 30, 1956, by H. E. D. Scovil.

The above initial reactants are heated in an alkali metal ditungstate flux, for example, sodium ditungstate, which may contain an excess of tungstic anhydride to further enhance the solubility of the divalent metal ion tungstates in the flux. Rather than initially using an alkali metal ditungstate, compounds that will react to form the alkali metal ditungstate may be used. For example, sodium tungstate and tungstic anhydride or sodium hydroxide and tungstic anhydride or tungstic acid react to form sodium ditungstate.

The initial mixture is equivalent to 10 to 75 mol parts of a divalent metal ion tungstate and 90 to 25 mol parts of the flux. As previously set forth, one advantage of the flux is its solvent power which permits lower temperatures to be used in forming a molten solution of the initial mixture. Therefore there is little interest in using a smaller amount of the flux which would necessitate the use of higher temperatures. A typical initial mixture containing 75 mol parts of calcium tungstate and 25 mol parts of the flux requires an approximate temperature of 1450° C. to form a molten solution. This temperature is a practical maximum temperature for most initial mixtures due to the volatilization temperatures of the initial components and economic considerations such as apparatus limitations and expense involved in achieving such elevated temperatures. Tungstic anhydride, for example, tends to volatilize above 1450° C.

The lower tungstate limit is determined by the eutectic point of the tungstate and flux solution. Below the eutectic point small flux particles tend to crystallize out of the molten solution when it is cooled before crystallization of the divalent metal ion tungstate crystals. The small flux particles act as nucleation centers around which the tungstate crystals grow. The eutectic point of a calcium tungstate-sodium ditungstate molten solution, a typical tungstate-flux solution, is approximately 10 mol parts calcium tungstate and 90 mol parts sodium ditungstate.

Since the size of the crystallized divalent metal ion tungstate crystals is dependent upon the amount of tungstate in the molten solution, the initial mixture preferably contains more than 10 mol parts of the desired tungstate. A preferred range is 20 to 75 mol parts of a divalent

metal ion tungstate in the initial mixture. Most desirably, the concentration of divalent metal ion tungstate is 30 to 75 mol parts.

The paramagnetic ion-containing substances in the initial mixture contain from 0.01 to 1.0 atom percent of the desired paramagnetic ion or ions based on the total divalent metal ions present. The desired paramagnetic ions are defined as those which are in the desired valency state. For example, 5 atom percent of iron may be incorporated into magnesium tungstate with the majority appearing as divalent iron and a limited amount falling within the prescribed limits as trivalent iron, the desired valency state for iron in this instance. The upper limit is governed by maser operation and efficiency. For example, it is known that beyond an optimum doping of the host crystal with paramagnetic ions, line broadening effects occur which detract from the amplification of the input signal. Still further doping of the host crystal results in complete maser breakdown. The lower paramagnetic ion limit is governed by the necessity of having sufficient unpaired electrons available to adequately amplify the input signal. A preferred paramagnetic ion limit is 0.02 to 0.5 atom percent of the desired paramagnetic ions based on the total divalent metal ions present.

It is desirable to have an excess of tungstic anhydride present in the initial mixture beyond any amount that is required to convert the initial components to the divalent metal ion tungstate and the alkali metal ditungstate flux. When an excess of tungstic anhydride is present in a molar amount up to the amount of divalent metal ion tungstate in the initial mixture, the solubility of the divalent metal ion tungstate in the alkali metal ditungstate flux is enhanced by the mechanism of the common ion effect. Such increased solubility lowers the temperature required to form a molten solution of the initial mixture. The addition of tungstic anhydride beyond the amount of divalent metal ion present has resulted in the crystallization of sheet like crystals containing approximately sixteen tungstate ions associated with each divalent metal ion.

There are no critical limits to particle sizes of the initial ingredients since a molten solution is formed of the initial mixture. Generally, the nonparamagnetic ion impurity limits are not critical. The amount of accidentally added paramagnetic impurity should not exceed the amount deliberately added. Preferably, the paramagnetic contamination should not exceed 0.1 the amount of the principal active paramagnetic ion intentionally added. Ordinary reagent grade chemicals were used in the following specific examples and are suitable as to both nonparamagnetic and paramagnetic impurity limits.

To minimize contamination, a crucible made of an inert material such as platinum is used to hold the initial mixture during processing. It is only necessary to heat the initial mixture until a molten solution is formed. This effect can readily be determined visually. Naturally, the higher the temperature, the shorter the heating time required to form a molten solution for a given concentration of initial components. The same effect can be achieved by using lower temperatures and longer heating times. The maximum permissible temperature is, in general, limited by the volatilization temperatures of the initial components and economic considerations such as apparatus limitations and expense of maintaining elevated temperatures. A practical temperature range for most mixtures is 900° C. to 1450° C. for up to five hours. Further firing is not harmful, however.

The atmosphere in which the heating is carried out is not critical. However, it is well known to use an oxygen-containing atmosphere such as air, oxygen, or oxygen plus an inert gas to prevent an ion in a higher valency state which is unstable at elevated temperatures from being reduced to a lower valency state. For example, the use of an oxygen-containing atmosphere is indicated when it

is desired to incorporate trivalent iron into a tungstate crystal this ion being unstable at elevated temperatures.

Similarly, although for convenience, atmospheric pressure is normally used, pressure is not critical. As is well known, increased pressures in general enhance solubility of the solute thereby permitting lower temperatures to be used. Additionally, in some instances, such elevated pressures retard volatilization permitting, if desired, increased temperatures to be used.

The molten solution is furnace cooled in the same atmosphere used in the heating step at a controlled rate until is solidifies forming the alkali metal ditungstate and divalent metal ion tungstate crystals having paramagnetic ions dispersed therein. It can readily be determined visually when solidification occurs. The temperature at which the molten solution solidifies naturally depends on the composition of the solution. For most of the contemplated molten solutions, cooling to a temperature of 650° C. to 800° C. is adequate to cause solidification. As is well known in the crystal growing art, the slower the molten solution is cooled, the larger the crystals that will be formed. The minimum cooling rate is determined both by economics and by the convenience of controlling small cooling rates. The maximum cooling rate is dictated by useful crystal sizes. In general, cooling rates of from about 0.1° C. per hour to 25° C. per hour have proven practical with an intermediate range of 0.5° C. per hour to 5° C. per hour and a preferred rate of 1° C. per hour.

The alkali metal ditungstate and the tungstate crystals may then be room cooled or quenched to room temperature and the sodium ditungstate removed from the tungstate crystals, for example, by washing the crystals with a strong alkali such as sodium hydroxide, potassium hydroxide or tetramethylammonium hydroxide. Other solvents for the alkali metal ditungstate which are not solvents for the tungstate crystals may be used.

Specific examples of divalent metal ion tungstate crystals containing small additions of paramagnetic ions grown by the methods of this invention are given below.

Example 1

15.3 grams of cadmium oxide, 0.029 gram of ferric oxide, 52.9 grams of sodium tungstate and 69.6 grams of tungstic anhydride were mixed together. The mixture was heated in a platinum crucible in air for four hours at a temperature of 1150° 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 sodium hydroxide leaving cadmium tungstate crystals doped with trivalent iron. Measurements made on these crystals are tabulated in Table I.

Example 2

20.5 grams of magnesium nitrate hexahydrate, 0.1 gram of chromium nitrate nine hydrate, 35.3 grams of sodium tungstate and 46.4 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above, using a temperature of 1250° C., with the resulting formation of magnesium tungstate crystals doped with chromium. Measurements made on these crystals are tabulated in Table I.

Example 3

92.5 grams of magnesium nitrate hexahydrate, 0.09 gram of ferric oxide, 129 grams of sodium tungstate and 185 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing detailed above using a temperature of 1150° C. with the resulting formation of magnesium tungstate crystals doped with trivalent iron. Measurements made on these crystals are tabulated in Table I.

Example 4

0.3 gram of ceric oxide, 47.2 grams of calcium nitrate

tetrahydrate, 117.6 grams of sodium tungstate and 139.2 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1250° C. with the resulting formation of calcium tungstate crystals doped with cerium.

Example 5

35.5 grams of calcium nitrate tetrahydrate, 0.03 gram of dysprosium oxide, 162 grams of sodium tungstate and 161 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above with the resulting formation of calcium tungstate crystals doped with dysprosium.

Example 6

47.2 grams of calcium nitrate tetrahydrate, 0.36 gram of terbium oxide, 117.6 grams of sodium tungstate and 139.2 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above with the resulting formation of calcium tungstate crystals doped with terbium.

Example 7

35.5 grams of calcium nitrate tetrahydrate, 0.03 gram of erbium oxide, 162 grams of sodium tungstate and 161 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above with the resulting formation of calcium tungstate crystals doped with erbium.

Example 8

47.2 grams of calcium nitrate, 0.01 gram of manganese carbonate, 117.6 grams of sodium tungstate and 139.2 grams of tungstic anhydride were mixed together. The mixture underwent the same processing as detailed above with the resulting formation of calcium tungstate crystals doped with manganese.

Example 9

35.5 grams of calcium nitrate tetrahydrate, 0.01 gram of gadolinium oxide, 162 grams of sodium tungstate and 161 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1150° C. with the resulting formation of calcium tungstate crystals doped with gadolinium. Measurements made on these crystals are tabulated in Table I.

Example 10

42.2 grams of strontium nitrate, 0.02 gram of gadolinium oxide, 117.6 grams of sodium tungstate and 139.2 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1200° C. with the resulting formation of strontium tungstate crystals doped with gadolinium. Measurements made on these crystals are tabulated in Table I.

Example 11

94.4 grams of calcium nitrate tetrahydrate, 0.035 gram of gadolinium oxide, 0.036 gram of ceric sulfate octahydrate, 0.017 gram of neodymium oxide, 116.0 grams of sodium tungstate and 200.0 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing detailed above using a temperature of 1250° C. with the resulting formation of calcium tungstate crystals doped with gadolinium, cerium and neodymium.

Example 12

39.2 grams of barium nitrate, 0.35 gram of europium oxide, 162.0 grams of sodium tungstate and 161 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing detailed above using a temperature of 1100° C. with the resulting formation of barium tungstate crystals doped with europium.

Example 13

41.8 grams of strontium nitrate, 0.35 gram of europium oxide, 117.5 grams of sodium tungstate, and 139.2 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed with the resulting formation of strontium tungstate crystals doped with europium.

Example 14

6.6 grams of zinc oxide, 0.02 gram of ferric oxide, 35.3 grams of sodium tungstate and 46.4 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1200° C. with the resulting formation of zinc tungstate crystals doped with trivalent iron.

Example 15

35.5 grams of calcium nitrate tetrahydrate, 0.006 gram of gadolinium oxide, 0.025 gram of ceric oxide, 162 grams of sodium tungstate and 161 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1100° C. with the resulting formation of calcium tungstate crystals doped with gadolinium and cerium.

Example 16

32.9 grams of zinc oxide, 0.50 gram of nickel carbonate, 145.4 grams of sodium tungstate and 208.7 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1250° C. with the resulting formation of zinc tungstate crystals doped with nickel.

Example 17

47.14 grams of calcium nitrate tetrahydrate, 0.04 gram of ytterbium oxide, 117.56 grams of sodium tungstate and 139.15 grams of tungstic anhydride were mixed together. The mixture then underwent the same processing as detailed above using a temperature of 1200° C. with the resulting formation of calcium tungstate crystals doped with ytterbium.

Whenever in the appended claims the terminology "initial ingredients equivalent to" is used, it is understood this means compounds that will react to form the desired divalent metal ion tungstate and the desired alkali metal ditungstate.

What is claimed is:

1. A process for growing single crystals of a divalent metal ion tungstate from initial ingredients equivalent to about 10 mol percent to about 75 mol percent MWO_4 where M is at least one divalent metal ion selected from the group consisting of magnesium, zinc, cadmium, calcium, strontium and barium, a flux comprising about 90 mol percent to 25 mol percent alkali metal ditungstate

and at least one paramagnetic ion-containing substance containing from about 0.01 atom percent to 1.0 atom percent of at least one paramagnetic ion based on the total divalent metal ions present selected from the group consisting of paramagnetic ions having atomic numbers 22 through 29 and 58 through 70, comprising heating said initial ingredients to a temperature sufficient to form a molten solution, cooling said molten solution at a rate of from about 0.1° C. per hour to 25° C. per hour until said molten solution solidifies forming divalent metal ion tungstate crystals and an alkali metal ditungstate, and removing said alkali metal ditungstate from said crystals.

2. The method in accordance with claim 1 wherein said flux contains sodium ditungstate and tungstic anhydride, the latter being present in an amount up to the amount of divalent metal ion tungstate on a mol basis.

3. The method in accordance with claim 1 wherein said molten solution is cooled at a rate of approximately 0.5° C. per hour to 5° C. per hour.

4. The method in accordance with claim 1 wherein said MWO_4 is calcium tungstate and said paramagnetic ion is gadolinium.

5. The method in accordance with claim 1 wherein said MWO_4 is strontium tungstate and said paramagnetic ion is gadolinium.

6. The method in accordance with claim 1 wherein said MWO_4 is cadmium tungstate and said paramagnetic ion is trivalent iron.

7. The method in accordance with claim 1 wherein said MWO_4 is magnesium tungstate and said paramagnetic ion is chromium.

8. The method in accordance with claim 1 wherein said MWO_4 is magnesium tungstate and said paramagnetic ion is trivalent iron.

9. Single crystal divalent metal ion tungstate grown by the method as defined in claim 1.

10. A three level maser device wherein the active maser material is a divalent metal ion tungstate having the composition as defined by claim 9.

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