

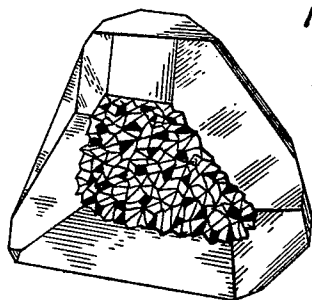
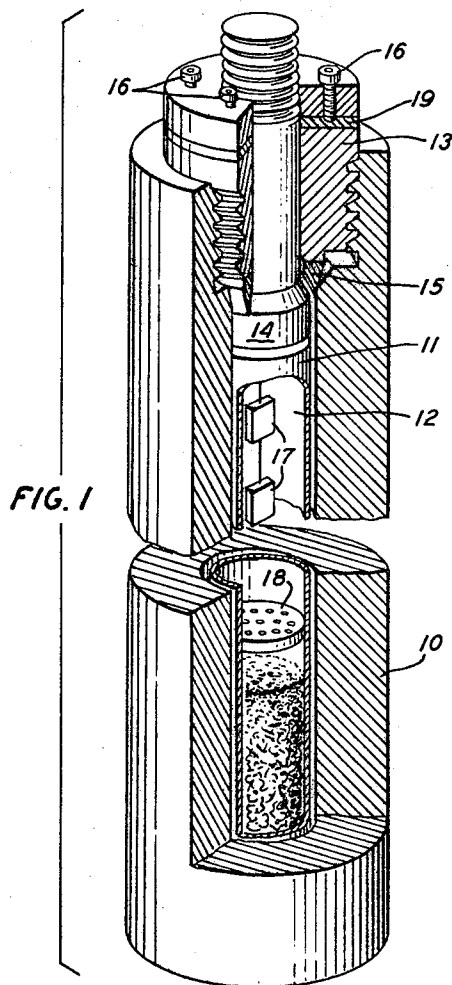
Feb. 17, 1970

E. D. KOLB ET AL
HYDROTHERMAL GROWTH OF MAGNETIC GARNETS
AND MATERIALS SO PRODUCED

3,496,108

Filed Nov. 15, 1966

2 Sheets-Sheet 1



E. D. KOLB
R. A. LAUDISE
E. G. SPENCER
D. L. WOOD
INVENTORS

BY

George S. Indig
ATTORNEY

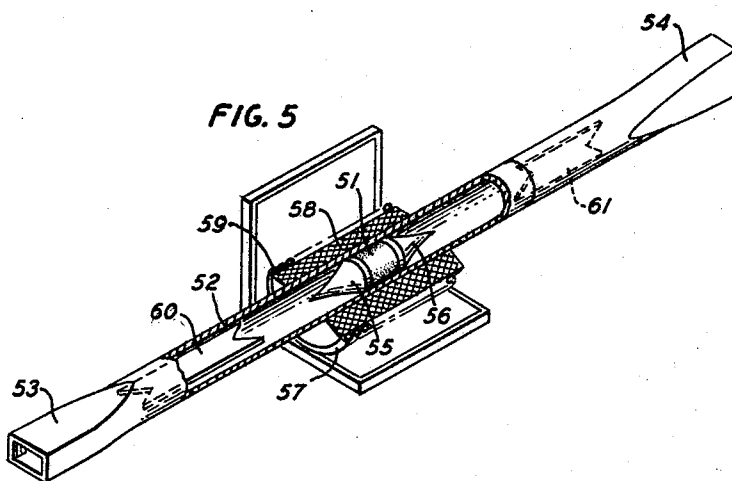
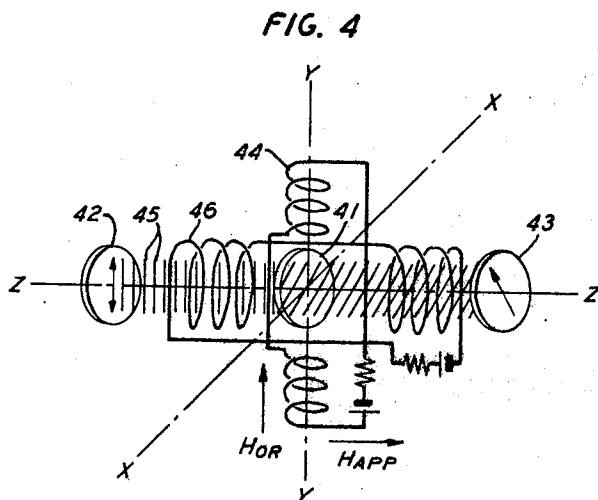
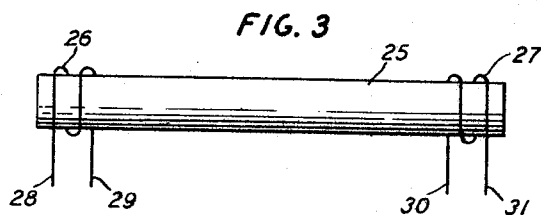
Feb. 17, 1970

E. D. KOLB ET AL
HYDROTHERMAL GROWTH OF MAGNETIC GARNETS
AND MATERIALS SO PRODUCED

3,496,108

Filed Nov. 15, 1966

2 Sheets-Sheet 2



1

3,496,108

HYDROTHERMAL GROWTH OF MAGNETIC GARNETS AND MATERIALS SO PRODUCED

Ernest D. Kolb, New Providence, Robert A. Laudise and Edward G. Spencer, Berkeley Heights, and Darwin L. Wood, Murray Hill, N.J., assignors to Bell Telephone Laboratories, Incorporated, Murray Hill, N.J., a corporation of New York

Filed Nov. 15, 1966, Ser. No. 594,612

Int. Cl. H01f 1/10; C04b 35/00; B01j 17/04

U.S. Cl. 252-62.57

7 Claims

ABSTRACT OF THE DISCLOSURE

YIG (yttrium iron garnet), as well as YIG containing as partial substituents any of the rare earths, aluminum, or gallium, is grown hydrothermally from a potassium hydroxide solution. Resulting crystals have excellent electrical and magnetic properties which are comparable with the best which have been measured on flux-grown crystals of the same composition. Where the solution is in deuterium oxide rather than water, special optical advantages result. These crystals may be used in microwave devices, delay lines and lasers.

BACKGROUND OF THE INVENTION**Field of the invention**

The invention is concerned with the preparation of single crystals of ferrimagnetic materials of the garnet structure. Such crystals are of interest in (1) microwave devices such as isolators, rotators, etc., generally based on gyromagnetic properties; (2) delay line and other elastic wave devices where they may act as their own transducers, based on magnetostrictive response to an applied magnetic field; and (3) in lasers, light modulators and related devices operating at wavelengths in the approximate range of from one to five microns. The physical size, crystalline perfection, and the electrical, magnetic and optical properties of the crystals grown by the invention recommend their use in this entire class of devices.

Description of the prior art

Crystals suitable for use in devices of the type described have in the past been grown only by flux techniques. Generally, these techniques involve spontaneous nucleation from a lead oxide-containing flux. Resulting crystals are ordinarily quite small, that is, of the order of a centimeter or less in maximum dimension. While certain such growth procedures regularly result in crystals having excellent device properties, they are quite costly, and certain uses, notably in delay lines, are virtually prohibited because of the practical inability to obtain requisite lengths. A recently described procedure involving the use of minor additions of silicon results in improved infrared transparency (37 JAP 1232 March 1966).

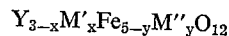
It is well known that seeded hydrothermal growth in general may result in the economic preparation of large, substantially unflawed crystals. In view of the widespread interest in YIG devices and the recognized shortcomings of flux growth, there has been extensive investigation into the development of a hydrothermal growth procedure. Solvent systems investigated include aqueous solutions of sodium carbonate (65 J. of Phys. Chem. 359, February 1961), as well as of sodium hydroxide (45 Am. Cer. Soc., 51, February 1962). Such attempts have met with general failure due either because crystallization of the proper phase did not occur or because the formed crystals had poor electrical characteristics, notably broad linewidths of the order of 30 oersteds (acceptable flux grown

2

crystals have linewidths of the order of an oersted or less). In consequence, there has been little or no activity in this field for the past three or four years, and it has been generally assumed that commercial preparation of YIG and related compositions would continue to utilize flux techniques.

SUMMARY OF THE INVENTION

In accordance with the invention, it is found that sound single crystals of YIG and partially substituted YIG may be hydrothermally grown on an immersed seed using a potassium hydroxide solution as the transfer medium. Ferrimagnetic resonance linewidths of an oersted and less have been measured, and magnetic and electrical properties are generally comparable to those of the flux-grown crystals. While for most uses an aqueous solution of potassium hydroxide is suitable, a further significant improvement in infrared transparency results from the substitution of deuterium oxide for water. Permitted compositions include 10 atom percent partial substitutions of one or more of the trivalent rare earth elements for yttrium as well as up to 25 atom percent partial substitution of gallium or aluminum for iron. Accordingly, a generalized formula may be expressed as follows:



where Y is yttrium, Fe is iron, O is oxygen, M' is at least one element selected from the trivalent rare earths Nos. 57 through 71, M'' is gallium and/or aluminum, x equals from 0 to 0.3, and y equals from 0 to 1.25.

Crystals resulting from use of the inventive procedures are suitably incorporated in devices depending for their operation on the electrical, magnetic, or acoustic properties of these materials. Such crystals and devices form a part of the invention.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a perspective view, partly in cross-section, of apparatus suitable for practice of the inventive processes;

FIG. 2 is a perspective view of a garnet crystal grown in accordance with a process herein;

FIG. 3 is a front elevational view of a delay line made from a hydrothermally grown crystal in accordance with the invention;

FIG. 4 is a diagrammatic representation of a light rotating device utilizing a garnet crystal in accordance with this invention; and

FIG. 5 is a perspective view, partly in section, of a microwave component containing an element made of a crystalline material grown in accordance with the invention.

DETAILED DESCRIPTION

Referring again to FIG. 1, there is depicted the now familiar modified Bridgman apparatus used for hydrothermal growth. The only significant difference from apparatus used for quartz growth is the inclusion of a precious metal liner of, for example, platinum, desirably incorporated because of the increased reactivity of the system. The main body 10 contains a precious metal can 11, so defining a chamber 12. A main nut 13 is threaded into the upper portion of the chamber. A plunger 14 is fitted into the bore 12 and is free to rise under the influence of pressure in the chamber. As the plunger rises, it contacts a steel seal ring 15 and is finally stopped by bearing against the main nut 13 through the seal ring. This action provides an effective seal for the growth chamber. The chamber is initially temporarily sealed by means of the set screws 16 which compress a resilient washer 19 against the shank of the plunger. The space between the can 11 and the inner wall of body 10 is filled

with water to a degree necessary to minimize pressure differential between the inside and outside of can 11.

For the growth procedure the chamber 12 is charged with nutrient material. The potassium hydroxide solution is added in the amount required to produce the requisite pressure at the desired operating temperature. Seed crystals such as 17 are suspended as shown. A baffle 18 may be interposed between the nutrient mass and the seed crystals so as to divide the chamber into two thermal zones. The baffle maintains a reliable temperature differential between the nutrient and the crystallization zone and expedites simultaneous growth of two or more seeds.

Chemically, the nutrient mass should be such as to yield the desired garnet composition. To produce YIG, the oxides Y_2O_3 and Fe_2O_3 are included approximately in the stoichiometric ratio of 3:5 mols, although deviation from this ratio by ± 10 mol percent is permitted. The transfer medium is a water solution or a deuterium oxide solution of potassium hydroxide, the permitted range of concentration being from 10 molal to 25 molal. The lower limit is dictated by (1) the fact that other phases appear at appreciably lower concentrations and (2) reduction in growth rate to inexpedient values at lower concentrations. If the base concentration is much higher than 25 molal, attack on the noble metal liner becomes a problem. The preferred concentration range is from 20–25 molal, the preferred lower limit being selected largely on the basis of growth rate.

The fill is desirably from 70 percent to 95 percent by volume although these limits are not absolute. For the permitted temperature range of from $350^\circ C.$ to $425^\circ C.$, the resulting pressures are such that a mechanical problem is introduced above 95 percent. The lower fill limit is based solely on growth rate, with rates dropping below a convenient level for lower fill. Temperatures are interrelated with the rates, so that temperatures above that indicated result in pressures which are unduly high for usual autoclave structures and with growth rate dropping unduly below the lower indicated temperature. While generally still higher temperatures are permitted for lower fills below the indicated minimum, there are some disadvantages in this procedure in that phases other than garnet tend to form. Still lower temperatures corresponding with still higher fill percentages do not generally result in acceptable growth rates. Pressures corresponding with these temperatures range from about 8,000 p.s.i. for $350^\circ C.$ and 70 percent fill to about 35,000 p.s.i. for $425^\circ C.$ and 95 percent fill.

As in any hydrothermal growth procedure, a significant parameter is the temperature differential between the seed and nutrient positions. The use of smaller differentials reduces the growth rate, but, in common with the choice of other parameters which minimize the rate, results in greater perfection due to the fact that more time is permitted for re-arrangement of atoms on the surface of the growing crystal. A minimum gradient of about $5^\circ C.$ is specified. This value arises from consideration of permissibly small growth rate and from the fact that temperature control of smaller gradients is generally difficult with commercially available apparatus. A preferred minimum of $10^\circ C.$ is recommended. The maximum tolerable gradient is considered to lie at about $50^\circ C.$ since for significantly larger values spontaneous nucleation becomes a problem. A preferred maximum lies at about $30^\circ C.$

Preferred seed plate orientation is (100). Growth also takes place on (211), (111), and (110) plates, although at somewhat lower rates. Growth rates as high as 12 mils a day have been observed for a 20 molal KOH solution, 80 percent fill, 390° crystallization temperature, and temperature differential of $10^\circ C.$ (8000 p.s.i.). As in other hydrothermal growth procedures, the temperature gradient is largely controlled by a baffle such as baffle 18 in FIG. 1. A convenient open area for the baffle is about 5 percent. Much larger than 10 percent open

tends to decrease the temperature gradient to values below that permitted in the usual apparatus.

Parameter ranges have been largely discussed in terms of crystal perfection and yield. In a preferred embodiment of the invention, parameters are set so as to result in optimum transparency for infrared frequencies. Various mechanisms resulting from certain impurity inclusions and from other deviation from stoichiometry was ordinarily responsible for increased absorption a wavelength near the one micron edge of the infrared window. It is indicated in JAP, supra, that deviations from the 3^+ valence state in iron results in increased absorption. In hydrothermal growth rather than flux growth, however, experimental information, while suggesting the undesirability of 2^+ or 4^+ impurities, assigns responsibility for increased absorption to a different mechanism.

Generally, hydrothermally grown crystals of garnet have not manifested significant absorption due to Fe^{2+} or Fe^{4+} but rather due to proton inclusion, that is due to OH or H_2O . The fundamental absorption for this inclusion occurs at about 2.8 microns, and the tail of this absorption or OH group overtone absorptions are sufficient to be of significance at infrared wavelengths well below that of the fundamental. This is not to say that 2^+ and 4^+ ion content should not be minimized, it appearing that the former is charge-compensated by protons and the latter tending to reduce growth rate. In general, absorption at 2.8 microns, attributed to proton inclusion, is minimized by maintaining the 2^+ ion content at a value below 100 p.p.m. by (1) using high purity Fe_2O_3 , Y_2O_3 and KOH, and (2) by eliminating H_2O in the transfer medium altogether.

Replacement of water by deuterium oxide results in an absorption not at 2.8 microns, but at 3.8 microns. While there are probably OD vibrations corresponding with the OH overtone absorption above this fundamental frequency, they too are frequency shifted toward longer wavelength. Garnets grown from D_2O rather than H_2O solution show significantly better transparency at wavelengths of from about 1 to 2 microns. Garnet crystals grown for optical uses at corresponding infrared frequencies are therefore desirably grown from D_2O rather than H_2O potassium hydroxide solutions. Crystals intended for such use are preferably also grown from high purity starting materials as indicated above.

The use of KOH, and, broadly, the invention is premised largely on its use, is required not only to maintain low values of absorption at 2.8 microns, but also to assure narrow ferrimagnetic resonance linewidth values. Linewidths of the order of 1 oersted and lower are regularly attained. For reasons not yet determined, there appears to be a correlation between low 2.8 micron absorption and narrow linewidth. For narrowest linewidth it is desirable to minimize proton inclusion, for example, by use of relatively low pressures and temperatures.

The following preferred examples describe specific parameters and compositions which have been utilized to produce some of the crystals which have been described.

Example 1

Apparatus similar to that depicted in FIG. 1 of approximate inner dimensions $7\frac{1}{2}''$ length by $1''$ diameter was utilized. 20 grams total of Y_2O_3 and Fe_2O_3 in the mol ratio of 3:5 were placed in the bottom of the autoclave. The baffle, such as that shown as element 18, was then placed in position. (100) seeds such as 17 were placed in the position shown. The autoclave was filled to 80 percent of its free volume, with 20 molal aqueous KOH. The autoclave was closed and was placed in a furnace where it was brought to a temperature of $375^\circ C.$ at the seed position in a period of about five hours. The bottom of the inner vessel corresponding with the nutrient position was at this point at a temperature of

5

about 400° C. (a temperature differential of about 25° C.). The pressure under these conditions was about 8000 p.s.i. Autoclave and contents were maintained under these conditions for a period of about 30 days, after which the autoclave was removed from the furnace, was permitted to cool to room temperature in a period of about 10 hours, after which it was opened and the seed crystals together with new growth removed.

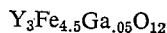
The resulting growth was of the order of 300 mils total (corresponding with a growth of about 10 mils a day). The measured ferrimagnetic linewidth was about 0.3 oersted. Infrared absorption was about 1.0 for $\alpha_{1.14\mu}$ and 4.0 for $\alpha_{2.8\mu}$ (α is defined as the extinction coefficient and equals $1/T \log (I_0/I)$, where T equals thickness in the transmission direction for the light beam being measured, I_0 equals beam intensity with crystal absent, and I equals beam intensity measured upon emergence from the crystal).

Example 2

The preceding example was repeated as described, however substituting D₂O for H₂O. Growth was about the same as noted. Linewidth was substantially unchanged. Transparency was improved to values of 0.5 for $\alpha_{1.14\mu}$ and 1.0 for $\alpha_{2.8\mu}$.

Example 3

The procedure of Example 1 was repeated; however, a fired and sintered mass of the composition



was used as the nutrient. The final hydrothermally grown crystal was of the same composition. The properties were about the same as noted in Example 1, but the crystal showed the lower saturation characteristic of garnet containing such substitutions.

These examples represent but a small number of those actually carried out. While, for simplicity, the first two examples are discussed in terms of the starting ingredients Y₂O₃ and Fe₂O₃, sintered nutrients such as those described in Example 3 or garnets prepared by hydrothermal recrystallization are generally to be preferred. To prepare hydrothermal crystals to be used as nutrient, it is expedient to set the operating parameters for maximum growth. The spontaneously nucleated crystals resulting under such conditions are quite suitable as nutrient.

The crystal shown in FIG. 2 was produced by growth on a (100) plate. It is seen that growth is normal to the seed and that the forming crystal begins to cap almost immediately. The particular crystal depicted still shows the rough thermodynamically unstable surface parallel to the rapidly growing seed plate.

The device of FIG. 3 is a ferromagnetic garnet delay line. This device consists of rod 25 of YIG or related material and encircling wire helices 26 and 27. Introduction of an electrical signal through leads 28 and 29 of helix 26 by means not shown produces an elastic wave by reason of the magnetostrictive response of rod 25. This wave is launched down rod 25, and upon attaining the position of encircling helix 27 produces an electrical signal which is read at terminals 30 and 31 by means of detecting apparatus not shown.

The device of FIG. 4 is illustrative of a structure designed to modulate an infrared beam through a magneto-optic interaction. In this device, body 41 is shown as a thin disc of YIG or a substituted garnet in accordance with this invention. The face of disc 41 is shown perpendicular to an axis designated the z axis. The disc lies in the plane of the orthogonal x and y axes, which are mutually orthogonal to the z axis. On either side of body 41 are mounted polarizing prism 42 and analyzing prism 43. Prism 42 is aligned to pass plane polarized light perpendicular to the x axis, and prism 43 is aligned as shown to pass only a component of the light in the absence of a modulating field. Coils 44, mounted on both sides of

6

garnet body 41 and along the y axis set up a direct-current magnetic field designated H_{or}. The field is sufficiently strong to saturate the ferrimagnetic body 41. The magnetization of garnet body 41 in such a direct-current field as H_{or} is aligned in the direction of the field. Coil 46 is energized to create a direct-current magnetic field H_{app}, in a direction parallel to the direction of propagation of light beam 15. Because of the presence of the magnetic field, H_{app}, the magnetization of the ferrimagnetic body 41 has a component in the direction of propagation of light beam 45. A rotation of beam 45 results upon passage through body 41, and analyzing prism 43 now passes a greater or lesser amount of light depending on the direction and magnitude of rotation. The device may include an amplitude-sensitive light detector not shown. For purposes of this figure, the rotation is shown as a clockwise rotation viewed from analyzing prism 43.

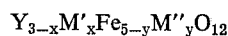
The structure of FIG. 4 is, of course, merely particularly exemplary and representative of a multitude of devices well known to those skilled in the art, any of which may beneficially utilize a crystalline body of any of the materials herein in a near infrared light system.

FIG. 5 depicts a Faraday rotation device which is intended to be exemplary of the wide range of microwave components in which crystals of this invention may be suitably employed. The device of FIG. 5 comprises element 51 composed of one of the crystals of this invention disposed in a circular wave guide 52. Two rectangular wave guides 53 and 54 are connected with circular wave guide 52 as shown. That portion of circular wave guide 52 containing element 51, which element is butted to tapered portions 55 and 56 which may consist of a dielectric material such as polystyrene, is encompassed by structure 57 comprising electrical winding 58 and cooling coil 59. Electrical winding 58 is energized by an electrical source not shown to produce a horizontal magnetic field in the region of element 51, the said field being sufficient to bias element 51 close to magnetic saturation. Radial vanes 60 and 61 are inserted for the purpose of absorbing reflections. For the device shown, vane 60 is so placed as to absorb horizontally polarized waves while radial vane 61 is so positioned to absorb vertically polarized waves. Tapered portions 55 and 56 are intended to reduce reflections so absorbed.

For expediency, the invention has been described in terms of a limited number of embodiments. Most notably, the growth procedures have been discussed as applied to YIG. However, it has been amply noted that these processes may be modified so as to substitute designated quantities of various ions for yttrium and/or iron. With regard to growth, invention is considered to reside in the discovery that device capability crystals of such garnet materials can, indeed, be grown hydrothermally providing potassium hydroxide is utilized as the transfer medium. Operating parameters and transfer compositions particularly useful for optimization of certain characteristics have been noted and constitute preferred embodiments of the invention.

What is claimed is:

1. Method for growing crystalline material consisting essentially of the composition



in which M' is at least one element selected from the trivalent rare earths, M'' is at least one element selected from the group consisting of gallium and aluminum, x equals from 0 to 0.3, and y equals from 0 to 1.25, which comprises disposing a crystal consisting essentially of the said composition and a mass of nutrient capable of yielding such composition in an alkaline solution within a closed vessel, heating said solution to a temperature of at least 350° C. while under a pressure exceeding its critical pressure, and maintaining a temperature difference between said seed and said mass of nutrient of at least 5° C. until a substantial increase in the size of said

crystal is obtained, characterized in that the said solution consists essentially of a 10 to 25 molal solution of potassium hydroxide in a solvent selected from the group consisting of water and deuterium oxide.

2. Method of claim 1 in which the said mass of nutrient comprises a sintered mass of the desired composition.

3. Method of claim 1 in which the said mass of nutrient comprises hydrothermally grown material.

4. Method of claim 1 in which the said solution consists essentially of a 20 to 25 molal solution of potassium hydroxide.

5. Method of claim 4 in which the said solvent consists essentially of deuterium oxide.

6. Method of claim 1 in which the said vessel is filled

to within 70 to 95 percent of its volume before heating.

7. Method of claim 1 in which the said temperature difference is within the range of from 10° C. to 30° C.

References Cited

UNITED STATES PATENTS

2,938,183	5/1960	Dillon	-----	252—62.57
3,156,651	11/1964	Geller	-----	252—62.57

10 ROBERT D. EDMONDS, Primary Examiner

U.S. Cl. X.R.

23—51, 52, 301, 305; 252—62.58