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HYDROTHERMAL GROWTH OF RARE EARTH ORTHOFERRITES AND
MATERIALS SO PRODUCED
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FIG. 1

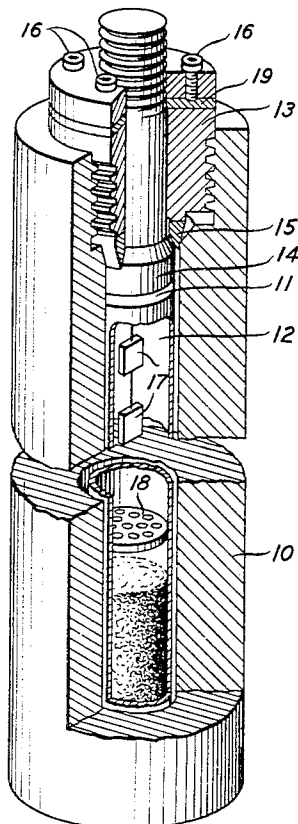


FIG. 2

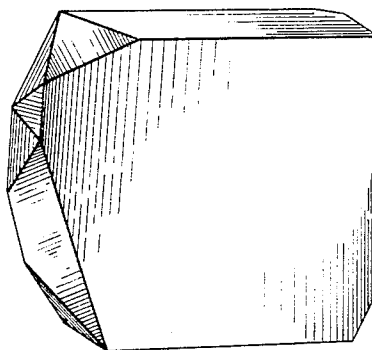
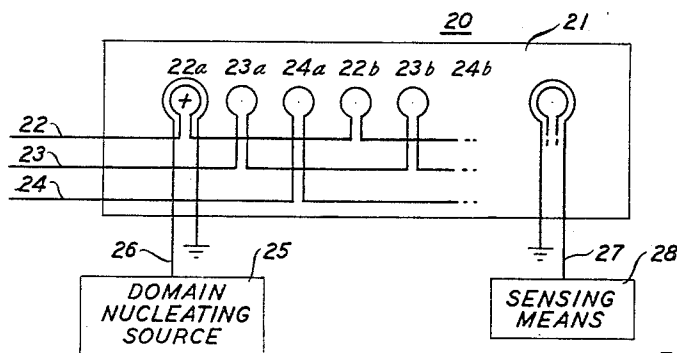


FIG. 3



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HYDROTHERMAL GROWTH OF RARE EARTH ORTHOFERRITES AND MATERIALS SO PRODUCED

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6 Claims

ABSTRACT OF THE DISCLOSURE

Rare earth orthoferrites including compositions containing mixed rare earths are 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 materials of the same compositions.

BACKGROUND OF THE INVENTION

Field of the invention

The invention is concerned with the preparation of single crystals of rare earth orthoferrites. Such crystals are of interest in a large class of devices including those which depend for their operation on the nucleation and propagation of single wall magnetic domains of restricted cross-sectional area.

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 such uses are virtually prohibitive because of the practical inability to obtain materials of substantial cross-sectional area.

SUMMARY OF THE INVENTION

In accordance with the invention, it is found that sound single crystals of both single and mixed rare earth and yttrium orthoferrites may be hydrothermally grown on an immersed seed using concentrated aqueous potassium hydroxide solution as the transfer medium. Magnetic and electrical properties are generally comparable to those of the flux-grown crystals. Crystals of single and mixed rare earth orthoferrite compositions grown by this technique are found to be physically sound and to evidence the requisite crystalline perfection for device use over cross-sectional areas of the order of one square centimeter and larger. A generalized formula of compositions grown in accordance with the inventive process may be expressed as follows:



where:

R is one or more of the elements of atomic numbers 39 and 62 through 70 of the Periodic Table of Elements (that is, yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium) and which may additionally contain from 0 to about 20 atom percent of elements numbers 57 through 60 (that is, from 0 to 0.2 in the formula of lanthanum, cerium, praseodymium or neodymium).

Generally, at least 80 atom percent of the R atoms should be selected from elements 39 and 62 through 70,

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as indicated, for the reason that growth of large crystals of orthoferrites becomes difficult for R atom ionic radii larger than that of samarium. It is known that lanthanum tends to go +4 and that europium tends to go +2 during orthoferrite growth. Retention of the trivalent state may be assured by the presence of hydrogen or other reducing agent and oxygen or other oxidizing agent, respectively.

The purpose for such cation variations has to do with device considerations, a complete discussion of which is not considered properly included in this description. Basically, however, a major class of device uses contemplated requires the nucleation and propagation of single wall domains. Desired bit density and other engineering considerations give rise to a requirement not only of domain stability and other obvious desiderata such as ease of nucleation, etc., but also to a desired domain size. It has been found that domain size, as well as certain other characteristics, depends, inter alia, on the proximity of the operating temperature to a transition temperature, notably to the spin flop transition temperature. Different rare earth inclusions give rise to different spin flop temperatures and consequently to a different range of domain sizes for given operating temperatures. Of the enumerated cations, only samarium gives rise to an orthoferrite composition having a spin flop temperature above room temperature. For certain types of operation, it is desired to operate single wall domain devices near the spin flop temperature. For such purposes samarium may be combined with one or more other cations to produce materials having a tailored spin flop temperature near any operating temperature.

Magnetically, the rare earth orthoferrites are canted antiferromagnetic. The magnetization and certain other magnetic properties depend on the canting angle and also on the degree to which the material is completely antiferromagnetic, that is, the extent to which the opposing moments are equal. Partial substitutions for iron, for example, with gallium or aluminum may result in a variation of the saturation magnetization, or in alteration of other magnetic properties. Device significance may follow, for example, from the fact that increased magnetization results in a decrease in stable domain size. Certain specific complete and partial substitutions have been outlined. Other variations, both in the rare earth and in the iron sites are feasible. Any such substitutions necessarily produce a concomitant change in magnetic properties. All substituted materials which retain the rare earth orthoferrite structure are desirably grown in accordance with the process of the invention and, in consequence, are considered within the inventive scope.

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 an orthoferrite crystal grown in accordance with a process herein; and

FIG. 3 is a schematic representation of a device depending for its operation upon the nucleation and propagation of single wall domains in a material of 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 ap-

paratus 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 chamber 12 and is free to rise with increasing 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 may be such as to yield the desired orthoferrite composition. To this end the starting materials may be rare earth oxide and iron oxide (Fe_2O_3) included approximately in the stoichiometric ratio although some deviation of up to about ± 10 percent is permitted. Alternatively, the nutrient may be pre-reacted in particulate or bulk form. Reacted nutrient may result from sintering or flux or hydrothermal crystallization. The transfer medium is a water solution of potassium hydroxide, the permitted range of concentration being from 10 molal to 25 molal. The lower limit is dictated by the facts that (1) other phases appear at appreciably lower concentrations and (2) reduction in growth rate to inexpedient values results from use of 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°C . to 425°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 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 the orthoferrite 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°C . and 70 percent fill to about 35,000 p.s.i. for 425°C . and 95 percent fill.

As in any hydrothermal growth procedure, a significant parameter is the temperature differential between the seed and nutrient. 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 rearrangement of atoms on the surface of the growing crystal. A minimum gradient of about 5°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°C . is recommended. The maximum tolerable gradient is considered to lie at about 50°C . since for significantly larger values spontaneous nucleation becomes a problem. A preferred maximum lies at about 30°C . The crystal structure of the rare earth orthoferrites is orthorhombic. Preferred seed plate orientation is $[110]$ or $[001]$. In general, growth rate is most rapid on the former. Use of an $[001]$ seed, however, is desirable for certain compositions and uses, since it results in an easy magnetization direction orthogonal to the crystal sheet. Growth rates as high as 6 mils a day have been observed for a 20 mole KOH solution, 80 percent fill, 375°C . crystallization temperature, and temperature differential of 30°C . ($\sim 8,000$ 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.

The following 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 $2\frac{3}{4}$ inch length by one inch diameter was utilized. 8 grams total of Fe_2O_3 and Yb_2O_3 in the mol ratio of 1:1 were placed in the bottom of the autoclave. The baffle, such as that shown as element 18, was then placed in position. $[110]$ 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°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 about 405°C . (a temperature differential of about 30°C .). The pressure under these conditions was about 8,000 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 180 mils total (corresponding with a growth rate of about 6 mils a day).

EXAMPLE 2

The preceding example was repeated as described, however, substituting presintered $\text{Fe}_2\text{O}_3 + \text{Yb}_2\text{O}_3$ for the starting materials indicated. The growth rate was substantially unchanged. The resulting crystal was about 1 cm. by 1 cm. by 210 mils and was sound and magnetically homogeneous.

EXAMPLE 3

The procedure of Example 1 was repeated, however substituting a sintered mass of the composition $\text{Sm}_6\text{Er}_4\text{FeO}_3$ for the nutrient therein indicated. The final crystal was of the same composition as that of the nutrient. Crystal size was of the order of 1 cm. by 1 cm. by 210 mils. Magnetic properties were of device caliber.

EXAMPLE 4

The procedure of Example 1 was repeated, however substituting a sintered mass of the composition YFeO_3 for the nutrient of that example.

EXAMPLE 5

The procedure of Example 1 was repeated, however substituting a sintered mass of the composition HoFeO_3 for the nutrient of that example.

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EXAMPLE 6

The procedure of Example 1 was repeated, however substituting a sintered mass of the composition TbFeO_3 for the nutrient of that example.

Products of Examples 3 through 6 were of the same composition as the starting material and were sound and magnetically homogeneous.

These examples represent but a small number of those actually carried out. All of the outlined compositions including single or mixed cations of elements 39 and 62 through 70, as well as compositions containing up to 20 atom percent of the other elements lanthanum and Nos. 58 through 60, as well as compositions containing other substituents permitted in the orthoferrite phase, are expediently grown without altering the outlined growth conditions.

The rare earth orthoferrites are desirably utilized in a class of devices which include a sheet or layer of a single crystalline material which is magnetically isotropic in the plane of the sheet and which has an easy direction out of the plane of the sheet. An exemplary use is in a shift register. The device of FIG. 3 is described in such terms.

In FIG. 3 a register 20 comprises a sheet 21 of a rare earth orthoferrite in accordance with the invention. The sheet is so oriented that at the operating temperature the preferred magnetization direction (easy direction) is normal to the plane of the sheet. Flux direction out of the paper as viewed is represented by a plus sign. Flux directed into the paper is represented by a minus sign. Conductors 22, 23, and 24, which may be deposited on the surface of sheet 21, form triplets of loops 22a, 23a, 24a; 22b, 23b, 24b, et seq. Loop size is somewhat smaller than the size of a corresponding stable single wall domain so that in operation any magnetized domain is partly within an adjoining loop. Such domains, once nucleated, for example, by means of a domain nucleating source 25 and loop 26, are stepped from loop position 22a to 23a to 24a to 22b and so forth by successive energization of conductors 22, 23, and 24 in that order by means not shown. Readout is accomplished by means of loop 27 and sensing means 28.

Other device uses include switches, other types of memory elements, logic elements, etc. Some such devices may operate at constant temperature at or near the spin flop temperature. Others may depend on a temperature variation sometimes local to flip the magnetization and so provide a means for easily nucleating a domain.

In other manner, the device description has been rudimentary. Devices of the type depicted in FIG. 3 have been developed to a far more advanced state. Some no longer utilize looped conductor configurations but depend upon the flux concentration which results from a sharp turn in the conductor pattern. A simple zig-zag pattern, for example, results in a bit location at each conductor reversal position. More generally, while present interest largely centers on the use of the materials of this invention in single wall domain elements, other devices may depend upon more conventional properties such, for example, as overall changes in magnetization, in changes in transmission properties of electromagnetic energy, under the influence of an applied field or with temperature change, of yielding the said material in an alkaline solution within ventive scope.

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It is clear from the description that most uses contemplate sheet material. Sheet material has been prepared by growth of a limited thickness on a seed as indicated in the examples. Subsequent treatment may include slicing and, finally, back sputtering to remove damaged portions. Crystals have also been grown epitaxially. Single crystal growth, of course, requires a substrate material having lattice dimensions closely approximating those of the orthoferrite to be grown. For device purposes, it is generally desired that the substrate be essentially nonmagnetic. The paramagnetic material terbium aluminate (TbAlO_3) has been found an appropriate substrate for the epitaxial growth of YbFeO_3 .

For expediency, the invention has been described in terms of a limited number of embodiments. In general, variations in growth conditions and grown compositions have been set forth. Also, it has been indicated that the device uses specifically described are merely exemplary. The invention is considered to reside in the finding that the use of aqueous KOH solutions in the indicated concentration range in a hydrothermal process results in the growth of large sound orthoferrite crystals.

What is claimed is:

1. Method for growing crystalline material which comprises disposing a crystal and a mass of nutrient capable of yielding the said material in an alkaline solution within a closed vessel, heating said solution to a temperature of at least 300°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 desired amount of crystalline growth results on said crystal, characterized in that the said solution consists essentially of a 10 to 25 molal aqueous solution of potassium hydroxide and in that the said crystalline material consists essentially of the composition RFeO_3 , where R is at least one element selected from the group consisting of yttrium samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and ytterbium, additionally containing from 0 to 20 atom percent of at least one element of the group consisting of lanthanum, cerium, praseodymium and neodymium.

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 1 in which the said vessel is filled to within 70 to 95 percent of its volume before heating.

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

References Cited

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