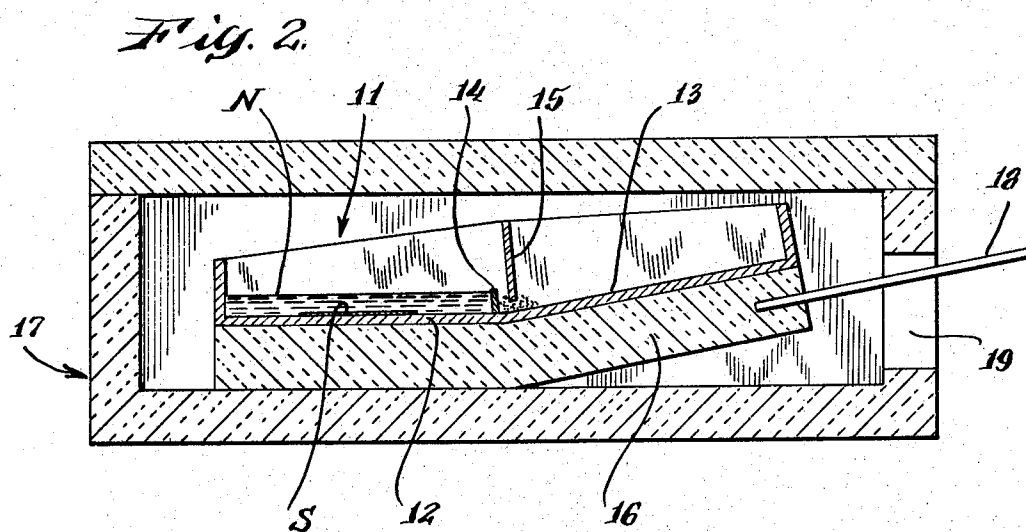
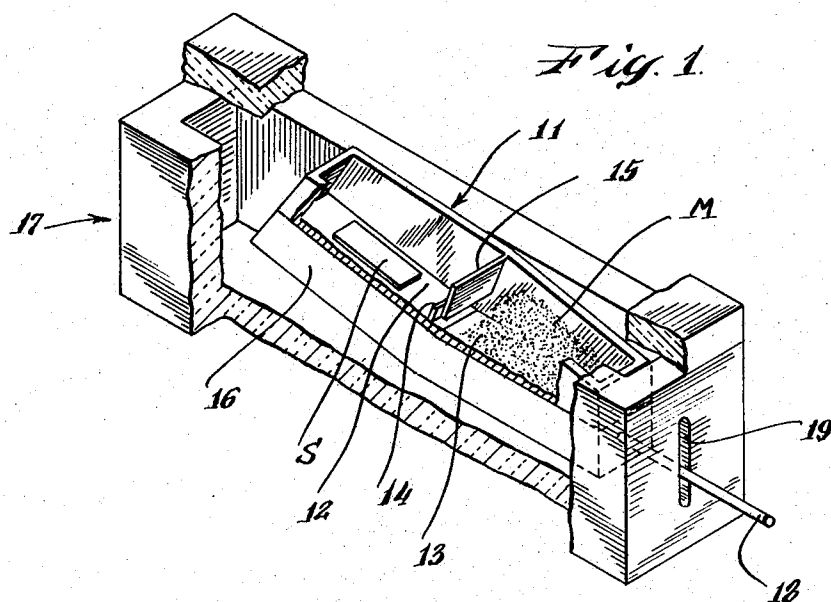


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METHOD OF GROWING A SINGLE CRYSTAL FILM OF
A FERRIMAGNETIC MATERIAL
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METHOD OF GROWING A SINGLE CRYSTAL FILM OF A FERRIMAGNETIC MATERIAL

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ABSTRACT OF THE DISCLOSURE

A flux method of growing single crystal thin films of a ferrimagnetic material which involves bringing a flux melt that is supersaturated with the ferrimagnetic material or its constituent components into contact with a single crystal oxide substrate and then moving the flux melt away from the substrate after the film has been grown. Some of the different ferrimagnetic materials that are grown include garnets, spinels and hexagonals.

This invention relates to ferrimagnetic materials. More particularly, this invention relates to a method of growing thin film single crystals of ferrimagnetic materials and to the article which is made up of a substrate and the thin film single crystal ferrimagnetic material that is so produced. Included amongst the different types of ferrimagnetic materials that can be grown are thin film single crystal ferrimagnetic garnets, ferrimagnetic spinels (spinel ferrites) and ferrimagnetic hexagonals (hexagonal ferrites).

Ferrimagnetism is basically a type of magnetism macroscopically similar to ferromagnetism but microscopically more like antiferromagnetism in that the magnetic moments of neighboring ions tend to align antiparallel. These moments are, however, of different magnitudes and hence may still have quite a large resultant magnetization.

The importance of ferrimagnetic materials is well established. These materials are, for example, extremely useful in microwave devices, magnetic transducers and magneto-optical devices. It has been found that single crystals of these materials show enhancement of certain magnetic properties associated with the polycrystalline material. For instance, the resonance lines of single crystals of these materials are much narrower than those found in the polycrystalline material, this property forming the basis of certain types of microwave devices.

It is also known that ferrimagnetic materials having a garnet type crystal structure are extremely useful in microwave devices. Ferrimagnetic garnets show the properties of Faraday rotation for microwaves and in transparent section can also be used to rotate visible light. Because of their magnetic properties, the coefficient of specific rotation is larger than in most other transparent materials.

Ferrimagnetic materials can be found in naturally occurring form. One example of such a material is magnetite.

In recent years, there has been considerable interest in growing synthetic single crystal compositions of different materials. Some of this activity has been directed toward the particular structure of the crystal grown whereas other activity has been directed toward the particular composition of the material. Much of the work in the latter area has centered around growing synthetic compositions of ferrimagnetic materials.

For example, in U.S. Patent No. 3,062,746, issued on Nov. 6, 1962, to R. B. MacCallum, a method is discussed for growing crystalline powders of ferrimagnetic materials in which the crystal has a garnet-like structure.

Other techniques for growing bulk single crystal garnets, some of which are ferrimagnetic are discussed in

U.S. Patent No. 2,957,827, issued on Oct. 25, 1960, to J. W. Nielson; U.S. Patent No. 3,050,407, issued on Aug. 21, 1962, to J. W. Nielson; and U.S. Patent No. 3,117,934 issued on Jan. 24, 1964, to R. C. Linares.

Still other techniques have been described for growing bulk single crystals of ferrimagnetic materials which are not solely limited to garnets. For example, in U.S. Patent No. 3,079,240 issued on Feb. 26, 1963, to J. P. Remeika, a method is described for growing bulk single crystals of ferrimagnetic garnets, orthoferrites and ferrites.

In the present invention, we are concerned with growing thin film single crystals of ferrimagnetic materials rather than bulk single crystals of ferrimagnetic materials as described in the above cited patents. Thin films of these materials would be very useful, for example, in microminiature circuitry.

In U.S. Patent No. 3,131,082, issued on Aug. 28, 1964, to J. R. Gambino, a method is discussed for growing a homogeneous solid phase rare earth iron garnet by vapor deposition which, according to Gambino, although polycrystalline in structure, exhibits ferromagnetic properties approaching that of a single crystal.

On the other hand, two different techniques for successfully growing thin film single crystals of synthetic garnets, some of which are ferrimagnetic are described in U.S. patent application Ser. No. 555,781, filed on June 7, 1966, by R. C. Linares and R. B. McGraw and assigned to the assignee of this application. One of the techniques described therein is a vapor deposition method. The other technique described therein is a flux growth method. Basically, the flux growth method involves lowering a single crystal substrate having certain characteristic properties into a molten salt flux which is supersaturated with a synthetic garnet material and then removing the substrate from the mixture after the film has been grown.

Although single crystal thin film garnets may be successfully grown by the flux growth method of Linares and McGraw, it has been found that in some instances some of the molten flux will cling to the substrate and film as it is being lifted out. When cooled, this can cause the substrate and film to crack. It has also been found that when lead fluxes are employed, undissolved particles of the garnet material will rise to the surface of the molten flux mixture and will also stick to the film as it is being lifted out. These particles may adversely affect the microwave and optical properties of the film that is grown.

Accordingly, it is an object of this invention to provide a new and improved method and apparatus for growing thin film single crystals of ferrimagnetic materials.

It is another object of this invention to provide a new flux growth method for growing single crystal thin films of ferrimagnetic materials.

It is still another object of this invention to provide a new method and apparatus for growing single crystal thin films of ferrimagnetic garnets, ferrimagnetic spinels and ferrimagnetic hexagonals.

It is yet still another object of this invention to provide a new method and apparatus for growing single crystal thin films of ferrimagnetic materials using a lead based flux.

It is another object of this invention to provide a new method and apparatus for growing single crystal thin films of synthetic garnets, spinels and hexagonals.

It is still another object of this invention to provide a new and novel article in the form of a substrate which is coated with a single crystal thin film of a ferrimagnetic material.

The above and other objects are achieved according to the method and apparatus of this invention.

Basically, the technique involved is a flux growth method in which a solution comprising a molten flux

(the solvent) that is fully saturated with a ferrimagnetic material (the solute) is moved into contact with the substrate. At least a part of the time in which the solution is in contact with the substrate the solution is caused to be supersaturated with the ferrimagnetic material. This may be achieved by cooling the solution. During this period of time the film will grow on the substrate. When the film so grown has reached the thickness desired, the solution is moved out of contact with the substrate. The coated substrate is then allowed to cool. Subsequently, the coated substrate is cleaned. The growing process is carried out in an oxidizing atmosphere. One feature of the invention involves moving the solution itself into and out of contact with the substrate rather than moving the substrate into and out of the solution. Another feature of the invention involves a novel constructed container for holding the materials and growing the film in the manner described above. Another feature involves the particular article that is produced. Other features include the particular materials used for the solvent, the solute and the substrate.

Other features and many attendant advantages of the invention will become apparent from the following detailed description when taken in connection with the drawings in which like reference numerals represent like parts and wherein:

FIGURE 1 is a perspective view of an apparatus for growing single crystal ferrimagnetic thin films according to this invention with the container which holds the materials and the substrate disposed in the furnace in one position; and

FIGURE 2 is a section view of the apparatus shown in FIGURE 1 in which the container is disposed in the furnace in another position.

Referring now to the drawings, and in particular FIGURE 1, there is shown a crucible or container 11 which is fabricated from platinum or other suitable noble metal. The container 11 may be provided with a cover (not shown). The container 11 has a pair of inwardly and downwardly slanting flat bottom surfaces 12 and 13 so that it can rest in either of two positions. The container 11 also has a pair of closely spaced parallel baffles 14 and 15. The baffles 14 and 15 are located in the container 11 in the vicinity of and parallel to a hypothetical plane which is the bisector of the bottom surfaces 12 and 13. One of the baffles 14 extends upward from bottom surface 12. The other baffle 15 extends downward almost to but does not touch bottom surface 13.

The container 11 is seated on a firebrick 16 which is disposed on the floor of a furnace 17. The furnace 17 may be, for example, electrically heated. The firebrick 16 is shaped to conform to the bottom of the container 11, and is provided with a detachable rod or handle 18 which extends out of the furnace 17 through a vertical slot 19.

Thus, by moving the rod 18 up or down (either manually or automatically) the container 11 can be shifted or tilted to either of two positions. In FIGURE 1, the container 11 is shown in one position whereas in FIGURE 2 the container is shown in the other position.

The method for growing the thin film is as follows:

The constituent materials M for growing a single crystal ferrimagnetic material along with a substrate S are loaded into the container 11. The constituent materials M comprise a solvent and a solute. Initially, the solvent and the solute may be in powder, crystal, ceramic or other similar form. The solvent or flux comprises any one or more of the various oxides or fluorides or combinations well known in the art that are used in growing crystals of ferrimagnetic materials. The solute which is a ferrimagnetic material comprises any of the magnetic oxides, component oxides of a magnetic oxide, or other compounds that will yield magnetic oxides when heated which are commonly used in growing ferrimagnetic crystals. The substrate is a single crystal oxide. The flux and the solute

are placed together at one end of the container 11, i.e., at bottom surface 13, while the substrate S is secured by any suitable means to the bottom of the container 11 at the other end, i.e., at surface 12. The particular composition and proportionate amounts of the flux and the solute and the properties of the substrate S will be described in more detail below with reference to specific examples. The container may, if desired, be covered.

The container 11 is then placed on the firebrick 16 in the furnace 17 so that it is resting on its bottom surface 13, that is, the surface which contains the constituent materials M.

The furnace 17 is then turned on and heated to a temperature at which the flux will become molten and which is high enough to dissolve at least some of the solute. The amount of solute that will dissolve is, of course, directly proportional to the temperature. However, the temperature should not be raised to a point at which the flux will vaporize excessively. The furnace 17 is held at that temperature a period of time to insure that all the solute that is capable of dissolving in the flux at that temperature has dissolved. At this point, the mixture is in the form of a solution N made up of a solvent fully saturated with the solute and in all probability some remaining undissolved solute.

The solution N is then moved into contact with the substrate S by tilting the container 11 to the position shown in FIGURE 2. At least most, if not all, of the undissolved solute is prevented by means of the baffles from reaching the other end of the container.

Either at the same time, or before, or after the solution N is moved into contact with the substrate S, the solution N is caused to be supersaturated with the solute. This is achieved by cooling the solution N. The cooling can either be controlled at a slow rate, i.e., a few degrees centigrade per hour or the furnace can simply be turned off. During this period of supersaturation, a single crystal thin film will grow on the substrate S.

Once the film has been grown to the desired thickness, the solution N is moved away from the substrate by shifting the container back to the position shown in FIGURE 1.

The furnace is then turned off, if this has not already been done, and the coated substrate is allowed to cool to room temperature. The coated substrate is then removed from the container 11 and cleaned.

Some of the single crystal thin film ferrimagnetic materials that can be grown by this method are ferrimagnetic garnets, ferrimagnetic spinels and ferrimagnetic hexagonals. Ferrimagnetic garnets have a cubic crystal structure that can be represented by the general formula



where A is yttrium or one of the rare earth elements having an atomic number between 62 and 71, B is trivalent iron or trivalent iron mixed with aluminum, gallium, scandium, chromium or cobalt and O is oxygen. Ferrimagnetic spinels have a cubic crystal structure and can be characterized by the formula MA_2O_4 where M is a divalent metal ion. A is a trivalent magnetic ion such as iron or chromium and O is oxygen. M may also be equal to .5 Li^{+} plus .5 Fe^{3+} . A may also contain small amounts of nonmagnetic trivalent ions. Hexagonal ferrites have a hexagonal crystal structure and can be in several different types. One type by way of example is characterized by the formula $BaFe_{12}O_{19}$ where Ba is barium, Fe is trivalent iron and O is oxygen. Other types of hexagonals also exist which are well known in the art.

When growing garnet films any of the well known fluxes used for making synthetic garnet crystals may be employed. Examples are barium borate, lead oxide, lead oxide-lead fluoride mixtures and lead borate. The solute may be any of the well known materials used in making synthetic ferrimagnetic garnet crystals. Examples are yttrium iron garnet crystal and a mixture of yttrium oxide and iron oxide. The substrate should be a single crystal gar-

EXAMPLE 1

A flux comprising powders of 3.5 grams of B_2O_3 , 90 grams of PbO , and 12 grams of Fe_2O_3 and a solute comprising 25 grams of $Y_3Fe_5O_{12}$ in crystal form was placed at one end of a platinum container. A substrate was placed at the other end of the container. The substrate was a $10 \times 10 \times .5$ mm. slab of $Gd_3Ga_5O_{12}$. The container was placed in a cold electrically heated furnace so that the flux-solute end was lower than the substrate end. The furnace was then heated to and held at $1050^\circ C.$ for two

hours. After this time, the container was tilted so that the solution flowed over and covered the substrate. At the same time the furnace was cooled at a rate of $400^\circ/hr.$ to $950^\circ C.$ At $950^\circ C.$ the container was tilted back so that the solution flowed off the substrate. The furnace was then turned off. After cooling to room temperature, the coated substrate was cleaned of any remaining flux by heating in hot dilute nitric acid. A single crystal thin film of yttrium iron garnet was thus grown on the substrate. In the above example and in each of the following examples, the substrate was a single crystal.

In each of the above examples, the film grown had a thickness of between one-tenth of a micron and 100 microns.

It should be noted that, if desired, single crystal thin films of ferrimagnetic materials having crystal structures different from those specified above may also be grown according to this invention.

Also, it is believed that in addition to the various fluxes enumerated above, it should be possible to use a flux made up of certain chlorides or combinations thereof.

Finally, it should be noted that although in all the examples described above, the single crystal substrate was nonmagnetic, a single crystal substrate that is magnetic could be used, if so desired.

What is claimed is:

1. A method of growing a single crystal film of a ferrimagnetic material comprising:

- (a) forming a melt comprising a molten salt flux saturated with a solute which on cooling will yield a single crystal of said ferrimagnetic material,
- (b) providing a single crystal oxide substrate,
- (c) bringing said melt and said substrate into contact with each other, and
- (d) cooling said melt causing said salt flux to be supersaturated with said solute,
- (e) moving said belt away from said substrate whereby a single crystal film of said ferrimagnetic material will be grown on said substrate.

2. The invention according to claim 1 and wherein bringing said melt and said substrate into contact with each other comprises pouring said melt over said substrate.

3. The invention according to claim 2 and wherein said film growing is carried out in an oxidizing atmosphere.

4. The invention according to claim 3 and wherein said melt and substrate are brought into contact with each other at approximately the same time as said melt is being cooled.

5. A method of growing a single crystal film of a ferrimagnetic material having a crystal structure selected from the group consisting of garnets, spinels and hexagonals comprising:

- (a) heating a crystal of the ferrimagnetic material to be grown and a salt flux to a temperature at which said flux becomes molten and fully saturated with said ferrimagnetic material,
- (b) providing a single crystal substrate,
- (c) immersing said substrate into said heated mixture,
- (d) cooling said heated mixture causing said salt flux to be supersaturated with said solute, and
- (e) decanting said heated mixture away from said substrate whereby a single crystal film of said ferrimagnetic material will be grown on said substrate.

6. A method of growing a single crystal film of a ferrimagnetic material having a crystal structure selected from the group consisting of garnets, spinels and hexagonals comprising:

- (a) heating the component parts of the ferrimagnetic material to be grown and a salt flux to a temperature at which said flux becomes molten and fully saturated with said component parts of ferrimagnetic material,
- (b) providing a single crystal substrate,

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TABLE I

Example:	Solute, grams	Flux (powder), grams	Substrate	Saturating temp., ° C.	Holding time at saturating temp., hours	Cooling rate, ° C./hr.	Growth temperature, ° C.	Film grown	Crystal structure
1	25 YIG (ceramic)	3.5 B_2O_3 , 90 PbO , 12 Fe_2O_3	$Gd_3Ga_5O_{12}$	1,050	4	400	950	$Y_3Fe_5O_{12}$	Garnet.
2	25 YIG (crystals)	3.5 B_2O_3 , 90 PbO , 12 Fe_2O_3	$Y_3Al_5O_{12}$	1,050	4	400	950	$Y_3Fe_5O_{12}$	Do.
3	15.9 Fe_2O_3 , 12.5 Y_2O_3 (powders)	3.5 B_2O_3 , 90 PbO , 12 Fe_2O_3	$Gd_3Ga_5O_{12}$	1,050	6	25	900	$Y_3Fe_5O_{12}$	Do.
4	6.36 Fe_2O_3 , 6.75 Y_2O_3 , 1.87 Ga_2O_3 (powders)	3.5 B_2O_3 , 90 PbO , 9.6 Fe_2O_3 , 2.8 Ga_2O_3	$Gd_3Ga_5O_{12}$	1,050	6	400	950	$Y_3Fe_5O_{12}$	Do.
5	3.2 NiO , 7.95 Fe_2O_3 (powders)	3 B_2O_3 , 100 PbO	$ZnAl_2O_4$	1,050	5	400	950	$NiFe_2O_4$	Spinel.
6	3.2 NiO , 7.95 Fe_2O_3 (powders)	3 B_2O_3 , 100 PbO	MgO	1,050	5	400	950	$NiFe_2O_4$	Do.
7	5.91 BeO , 28.68 Fe_2O_3 (powders)	150 PbO	Al_2O_3	1,050	5	50	950	$PbFe_2O_9$	Hexagonal.
8	40 Fe_2O_3 (powder)	100 PbO	Al_2O_3	1,050	5	50	950	$PbFe_2O_9$	Do.

net. Examples are gadolinium gallium garnet and yttrium aluminum garnet.

When growing spinel ferrites, typical fluxes that may be used are barium borate, lead oxide and lead borate. Examples of ferrimagnetic materials that can be used as the solute are nickel ferrite and a mixture of nickel oxide and iron oxide. Examples of substrates that may be used include magnesium aluminate, zinc aluminate and magnesium oxide. The substrate should be a single crystal.

When growing hexagonal ferrites, typical fluxes that may be used are lead oxide, barium borate, sodium carbonate

- (c) bringing said heated mixture and said substrate into contact with each other,
- (d) cooling said heated mixture causing said salt flux to be supersaturated with said solute, and
- (e) decanting said heated mixture away from said substrate whereby a single crystal film of said component parts of ferrimagnetic material will be grown on said substrate.

7. A method of growing a single crystal thin film of a ferrimagnetic material having a crystal structure selected from the group consisting of garnets, spinels and hexagonals comprising:

- (a) immersing a single crystal oxide substrate in a melt of materials which on cooling will yield a single crystal ferrimagnetic material having the desired crystal structure,
- (b) cooling the melt causing said melt to yield a single crystal of said ferrimagnetic material and which will grow as a film on said substrate, and
- (c) decanting the melt away from the substrate after a film of the desired thickness has been grown.

8. The method according to claim 7 in which said single crystal thin film is a garnet and wherein said melt consists essentially of $Y_3Fe_5O_{12}$, B_2O_3 , PbO and Fe_2O_3 , and said substrate is $Gd_3Ga_5O_{12}$.

9. The method according to claim 7 in which said single crystal thin film is a garnet and wherein said melt consists essentially of $Y_3Fe_5O_{12}$, B_2O_3 , PbO , and Fe_2O_3 , and said substrate is $Gd_3Ga_5O_{12}$.

10. The method according to claim 7 in which said single crystal thin film is a garnet and wherein said melt consists essentially of $Y_3Fe_5O_{12}$, B_2O_3 , PbO , and Fe_2O_3 , and said substrate is $Y_3Al_5O_{12}$.

11. The method according to claim 7 in which said single crystal thin film is a garnet and wherein said melt consists essentially of Fe_2O_3 , Y_2O_3 , B_2O_3 , PbO , and said said substrate is $Gd_3Ga_5O_{12}$

12. The method according to claim 7 in which said single crystal thin film is a garnet and wherein said melt consists essentially of Fe_2O_3 , Y_2O_3 , B_2O_3 , PbO , Fe_2O_3 , and Ga_2O_3 , and said substrate is $Gd_3Ga_5O_{12}$.

13. The method according to claim 7 in which said single crystal thin film is a spinel and wherein said melt consists essentially of NiO , Fe_2O_3 , B_2O_3 , and PbO and said substrate is $ZnAl_2O_4$.

14. The method according to claim 7 in which said single crystal thin film is a spinel and wherein said melt consists essentially of NiO , Fe_2O_3 , B_2O_3 , and PbO and said substrate is MgO .

15. The method according to claim 7 in which said single crystal thin film is a hexagonal and wherein said melt consists essentially of $BaCO_3$, Fe_2O_3 , and PbO and said substrate is Al_2O_3 .

16. The method according to claim 7 in which said single crystal thin film is a hexagonal and wherein said melt consists essentially of Fe_2O_3 and PbO and said substrate is Al_2O_3 .

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