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3,386,799

GROWTH OF YTTRIUM IRON GARNET

William H. Grodkiewicz, Murray Hill, and Le Grand G. Van Uiter, Morris Township, Morris County, N.J., assignors to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York
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This invention relates to a method for the growth of single crystal yttrium iron garnet in a flux comprising lead fluoride and boron oxide, or mixtures thereof with lead oxide to which calcium oxide has been added.

Yttrium iron garnet is ferrimagnetic in nature, evidences the property of Faraday rotation for microwaves and in transparent sections can be used to rotate light. As is well known in the art, single crystal ferrimagnetic materials manifest enhancement of certain magnetic properties associated with the polycrystalline material. In particular, the resonance lines of single crystal materials are much narrower than those found in the polycrystalline material, this property forming the basis for the types of microwave devices described in United States Patents 3,013,229 and 3,016,495.

A convenient prior art technique for growing yttrium iron garnet involved combining the reactants in proper proportions with a flux comprising lead fluoride and boron oxide or mixtures thereof with lead oxide, heating the mixture to form a homogeneous melt and obtaining the single crystal material from the molten bath by conventional crystallization procedures.

The present invention embodies the same general procedures as the aforementioned crystal growing method with the exception that calcium ions are added to the melt in certain critical proportions. The use of the calcium ions is advantageous in several respects, the most important being the enhancement in the degree of reproducibility as well as a significant increase in the size of the garnet crystal obtained as compared with those obtained by the prior art technique, such increase being up to an order of magnitude and greater. Additionally, a marked enhancement in optical clarity results from the use of the described technique.

An important aspect of the present invention lies in the use of specific flux compositions, for example, those containing critical percentages of lead oxide, lead fluoride and boron oxide. In the growth of yttrium iron garnet as described, it is essential that the weight percent of lead oxide in the flux range from 0-60 and the weight percent of lead fluoride range from 100-40 (based upon a lead oxide-lead fluoride flux), so corresponding with weight ratios of lead oxide to lead fluoride ranging from 0 to 1.5 to 1. Additionally, there is added to the flux composition boron oxide in an amount ranging from 0.5 to 5.0 weight percent based on the weight of the lead oxide-lead fluoride composition which corresponds with weight ratios of $B_2O_3/PbO+PbF_2$ ranging from 1:20 to 1:200. The preferred range is from 1:28.5 to 1:66.6. An optimum range has been found to correspond with the range from 1:35.7 to 1:45.4.

It has been determined that the use of a ratio of lead oxide to lead fluoride of greater than approximately 1.5:1 results in an increased incidence of orthoferrites, so increasing the difficulty of separation of yttrium iron garnet therefrom. Studies on the growth of yttrium iron garnet ($Y_3Fe_5O_{12}$) with various flux component ratios have extended down to a lead oxide to lead fluoride ratio of zero at which there is a noticeable decrease in crystal perfection. A preferred weight ratio range of PbO/PbF_2 has been found to correspond with the approximate ratios of 1:3 to

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1.22:1 whereas an optimum range has been found to correspond with the approximate ratios of 1:1.5 to 1:1.04.

It has been further determined that the use of a ratio of $B_2O_3/PbO+PbF_2$ less than 1:200 does not provide the requisite B_2O_3 to effectively suppress $Y_3Fe_5O_{12}$ nucleation under the operating conditions of the process whereas ratios greater than 1:20 tend toward excessive supersaturation which may lead to the spontaneous nucleation of far too many crystals to permit garnet growth to a crystal of appreciable size, from one to three crystals per run being preferable since they will be larger and contain most of the available crystal material.

The general procedure for crystallization processes involving the garnet system employs 1300° C. as the upper limit of temperature. This limitation is set by reason of considerations pertaining to volatility of ingredients in the melt, changing composition of the flux, as well as by reactions with crucible materials, such as platinum, at temperatures substantially in excess of this limit and for various practical reasons such as apparatus limitations. The lower temperature limit of the system during crystallization in the $Y_3Fe_5O_{12}$ system is determined by the observed re-resolution of the crystals in the solvent at temperatures substantially lower than about 950° C., although this limit is determined by a most favorable flux composition and is somewhat increased by varying from this optimum. It is possible to avoid re-resolution by a relatively rapid cooling of the flux from this minimum temperature to a complete solidification.

Optimum cooling rates over the crystallization range of from about 1300° C. to 950° C. are determined by the usual criteria, the faster the rate of cooling, the greater the number of nucleation centers with a consequent decrease in crystal size and vice versa. Cooling rates may vary from as low as ½° C. per hour or lower to as high as 10° C. per hour. It is generally desirable to cool as slowly as possible to secure the largest possible crystal size and, consequently, a cooling rate of as low as ½° C. per hour is most desirable.

For the fluxes described, it is desirable to operate at the approximate nutrient to flux weight ratios within the range of 1:2 to 1:12.5. Operation with the lesser nutrient concentration (1:12.5) results in the initiation of nucleation at a somewhat lower temperature, and since it has little effect on the minimum (dependent on re-resolution temperature) results in an overall decrease in the temperature range of crystallization, with a resultant decrease in crystal size. Operation of the process at a more concentrated ratio (above about 1:2) results in an increase in the number of nucleation centers for a given cooling rate with a consequent loss in control. Nucleation can be minimized in the more concentrated melts by adding single crystal seeds to the mixture. The powdered crystal components are dissolved first upon heating and the added crystal dissolves much more slowly. Under controlled conditions a seed will survive when the melt is at equilibrium and act as a growth center during cooling. Under non-seeded conditions, a preferred nutrient to flux weight ratio range is from 1:2.5 to 1:10, an optimum ranging from 1:3.3 to 1:8. Under seeded conditions approximately 2 to 3 times the optimum concentration of materials is employed.

As noted above, the formula for yttrium iron garnet is $Y_3Fe_5O_{12}$, so indicating a molecular ratio of three parts of yttrium to five parts of iron. Operation of the process with the ratio indicated by the stoichiometric materials has been found effective; however, it has been found helpful to employ an excess of iron ranging up to 100 percent beyond stoichiometry. The preferred range is from 10 to 30 percent beyond stoichiometry. An

optimum range has been found to correspond with the range of from 15-25 percent beyond stoichiometry.

mately 20 grams in size were produced. The optical clarity of these crystals proved to be poor.

TABLE

Example	Starting Ingredients (Grams)	Flux Composition (Grams)			Product	Yield (Grams)	Crystal Size, Maximum Dimensions (CMS)
		PbO	PbF ₂	B ₂ O ₃			
1	Y ₂ O ₃ , 1,694; Fe ₂ O ₃ , 2,397; CaO, 4.0	6,021	4,926	279	Y ₃ Fe ₅ O ₁₂	2,300	2.5" long; 280 grams, several 200 grams; medium transparency.
2	Y ₂ O ₃ , 1,694; Fe ₂ O ₃ , 2,397; CaO, 40.0	6,021	4,926	279	Y ₃ Fe ₅ O ₁₂	2,500	2" long; 250 grams, several 200 grams; high transparency.

In accordance with the inventive technique, it has been determined that the addition of calcium ions to the melt, typically in the oxide form, in an amount ranging from 0.05 to 5.0 weight percent CaO of the crystal components in the melt results in a marked increase in crystal size, improves the optical clarity of the resultant crystal and enhances reproducibility. This range is found to correspond with a range of from 0.001 to 0.05 gram atoms of calcium per formula weight of Y₃Fe₅O₁₂. It has been found that the use of quantities less than the noted 0.05 weight percent minimum fails to result in significantly increased crystal size whereas excesses of calcium oxide beyond the 5.0 weight percent limit fail to further enhance crystal size and merely create practical problems. Best results are obtained by using at least 0.1 weight percent of calcium oxide and preferably at least 1 weight percent.

Examples of the application of the present invention are set forth below. They are intended merely as illustration and it is to be appreciated that the processes described may be varied by one skilled in the art without departing from the spirit and scope of the invention.

The examples are in tabular form for convenience and brevity. Each set of data in the table is to be considered as a separate example since each set of data was obtained in a separate process. The procedure followed in the examples is as follows:

A mixture of the starting materials was weighed into a platinum crucible and sealed with a platinum lid. The crucible was next placed into a "Globar" furnace with refractory muffle. For expediency, the furnace was preheated to 1300° C. The crucible, together with its contents, was then permitted to attain a temperature of 1300° C. and maintained at this temperature for a period ranging from 1-24 hours. The resultant crystals were chemically analyzed and magnetic measurements made on the washed product. These measurements, not considered to be within the scope of this disclosure, were in conformity with observed magnetic properties on other specimens of these compositions.

For comparative purposes the procedure of Examples 1 and 2 was repeated in the absence of CaO. In both cases, it was found that a few small crystals, approxi-

While the invention has been described in detail in the foregoing specification, the aforesaid is by way of illustration only and is not restrictive in character. The several modifications which will readily suggest themselves to persons skilled in the art are all considered within the scope of this invention, reference being had to the appended claims.

What is claimed is:

1. A method for growing crystals of Y₃Fe₅O₁₂ of substantial size, which comprises establishing a melt of a nutrient, comprising the constituent components of said crystals and containing CaO in an amount ranging from 0.05 to 5 percent by weight of said components, together with a flux selected from the group consisting of (a) lead fluoride and boron oxide and (b) lead fluoride, boron oxide and lead oxide and cooling the resulting melt until crystals of Y₃Fe₅O₁₂ are found, the weight ratio of lead oxide to lead fluoride in the flux ranging from 0 to 1.5:1, the amount of boron oxide in said flux being such that the weight ratio of B₂O₃/PbO+PbF₂ ranges from 1:20 to 1:200, the nutrient to flux weight ratio ranges from 1:2 to 1:2.5, and said cooling is conducted at a rate of about ½° C. to 10° C. per hour.

2. A method in accordance with the procedure of claim 1 wherein CaO is present in an amount of approximately 1.0 percent by weight of the constituent components of said Y₃Fe₅O₁₂.

3. A method in accordance with the procedure of claim 1 wherein CaO is present in an amount of approximately 0.1 percent by weight of the constituent components of said Y₃Fe₅O₁₂.

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OSCAR R. VERTIZ, Primary Examiner.

HERBERT T. CARTER, Examiner.