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GARNET GROWTH FROM BARIUM OXIDE-BORON OXIDE FLUX

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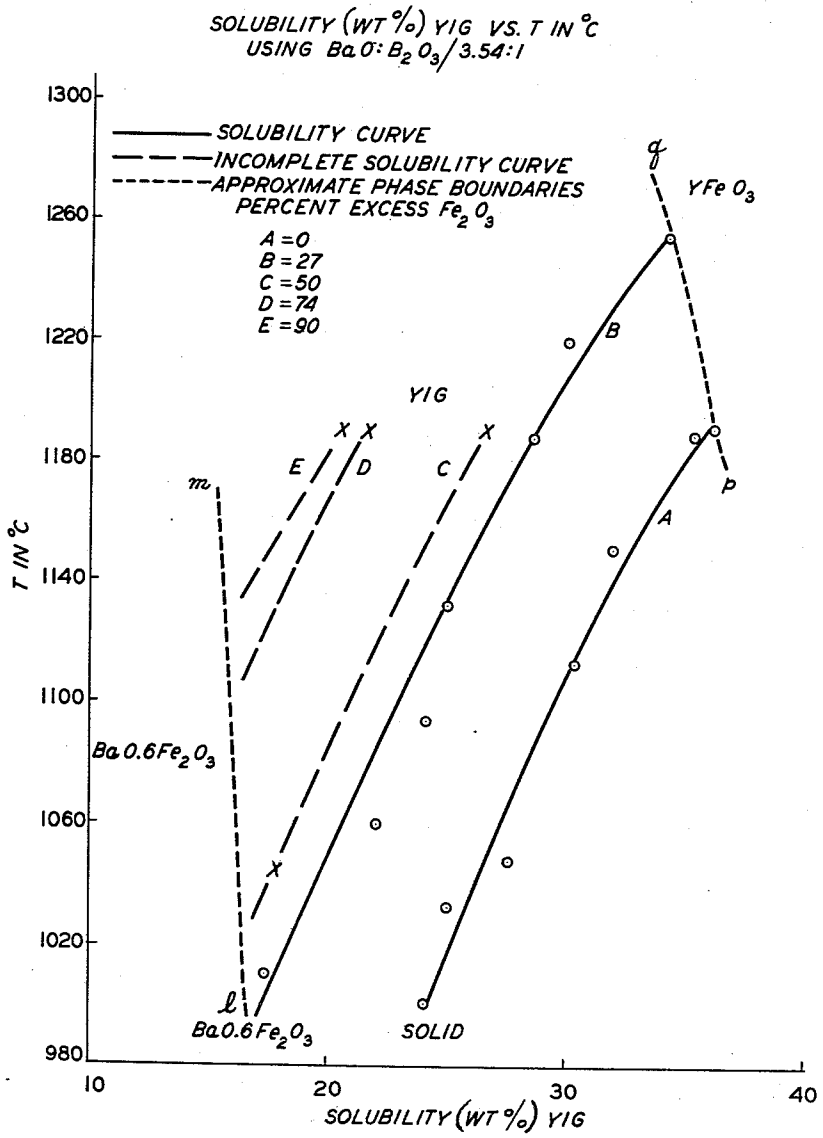

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GARNET GROWTH FROM BARIUM OXIDE-BORON OXIDE FLUX

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This invention relates to a method for growing single crystals of synthetic garnet in a flux comprising barium oxide-boron oxide. The synthetic garnet materials considered here can be represented by the formulas $M_3Me_5O_{12}$ or $M_3Me_2(MeO_4)_3$, where O is oxygen, Me is a trivalent metal and M is yttrium or one of the rare earth elements of atomic number between 62 and 71 or a mixture of these rare earth elements with each other or with yttrium. Me may be at least one of the elements trivalent iron, gallium, scandium, chromium or cobalt.

As is well known in the art, single crystals of ferrimagnetic material show 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 copending application Serial No. 778,352, filed December 5, 1958, now U.S. Patent 3,016,495, issued on January 9, 1962, to P. K. Tien, and Serial No. 774,172, filed November 17, 1958, now U.S. Patent 3,013,229, issued on December 12, 1961, to R. W. De Grasse. A convenient prior art method for producing such single crystals consisted of combining the reactants in proper proportions with a flux consisting of lead oxide, heating the mixture to form a homogeneous liquid, and forming the single crystals from a molten bath by standard crystallization procedures. This technique is discussed in detail in U.S. Patent 2,957,827, issued October 25, 1960, to J. W. Nielsen.

The present invention embodies the same general procedures as the aforementioned crystal growing methods with the exception of the flux employed. The present inventive method utilizes a flux comprising barium oxide and boron oxide. The use of such a flux is advantageous in several respects, the most important being that garnet growth may occur in a nontoxic congruently saturating system.

An understanding of the invention is facilitated by reference to the drawing in which

The FIGURE is a graphical representation on coordinates of temperature in degrees centigrade against solubility in weight percent of yttrium iron garnet showing the solubility curves of various compositions of yttrium oxide and ferric oxide in a barium oxide-boron oxide flux ratio of 3.54:1.

An important aspect of the present invention lies in the use of specific flux ratios, that is, critical ratios of barium oxide to boron oxide. In the growth of the garnet structures discussed above it is essential that the weight ratio of barium oxide to boron oxide be within the range of 3.16:1 to 4.55:1. It has been found that the use of a ratio of barium oxide to boron oxide of less than about 3.16:1 results in the formation of barium ferrite, so decreasing the yield of the desired crystal and increasing the difficulty of separation of this material

from the desired garnet. Studies on the growth of garnets with this flux have extended up to ratios of 4.55:1 at which point orthoferrites begin to form. An optimum ratio has been found to be 3.54:1.

The general procedure for crystallization processes involving the garnet systems generally employs 1300° C. as the upper limit of temperature. This limitation is set by reason of considerations pertaining to volatility of ingredients in solution, and changing composition of flux et cetera.

The present inventive technique permits crystallization of the garnet structures discussed above from a congruently saturating system, that is, one in which stoichiometric amounts of nutrient are employed. However, the barium oxide-boron oxide system is not limited to stoichiometric concentrations when trivalent iron is present and excesses of ferric oxide up to 90 percent may be employed.

This fact may best be illustrated by reference to the figure wherein there is shown a graphical representation on coordinates of temperature in degrees centigrade against solubility in weight percent of yttrium iron garnet, which indicates the crystallization ranges for various compositions of yttrium oxide and ferric oxide from stoichiometric to about 90 percent excess of ferric oxide in a 3.54:1 BaO to B_2O_3 flux. Curve A represents stoichiometric quantities of yttrium oxide and iron oxide and it is noted that the crystallization temperatures vary from about 1180° C. to about 995° C. Curve B represents the optimum for crystallization ranges in the system discussed and indicates that a flux containing an excess of 27 percent ferric oxide has the greatest crystallization range, namely, 1255 to 990° C. Curves C, D, and E represent incomplete solubility curves for solutions containing up to 90 percent excess ferric oxide. It is noted that lines LM and PQ define the precise ranges in which the process can be operated without producing the unwanted barium ferrite and yttrium orthoferrite.

Thus, the temperature range for garnet growth may vary over the range of 1255° C. to 990° C. dependent upon the particular materials and concentrations employed as discussed above.

Optimum cooling rates over the crystallization range of from about 1255° C. to 990° C. are determined by the usual criteria, the faster the rate of cooling, the greater 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 20° 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.

Ideal nutrient concentration increases with increased boron. It is desirable for a 3.54:1 flux to operate at the approximate nutrient to flux weight ratio of 1:2. However, variations over the range of ratios may be used from 1:1.8 to 1:4.5. Operation with the lesser nutrient concentration (1:4.5) results in the initiation of nucleation at a somewhat lower temperature and results in an overall decrease in the temperature range of crystallization with a resultant decrease in yield. Operation at a more concentrated ratio than 1:1.8 results in an increase in the number of nucleation centers for a given cooling, with a consequent loss in control and may not result in a yield

commensurate with the increased concentration of starting ingredients.

The preparation of crystalline compositions of the entire range intermediate the two materials, yttrium iron garnet and gadolinium iron garnet are feasible.

In the growth of gadolinium iron garnet the considerations discussed relative to yttrium iron garnet apply. Accordingly, the barium oxide to boron oxide ratio in the flux and also the preferred range discussed is suitable. The maximum temperature of 1255° C. is the same for the various reasons described.

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

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

A mixture of the starting materials was weighed into a 100 cubic centimeter platinum crucible and sealed with a platinum lid. The crucible was next placed into an electrically-heated furnace, was heated to a temperature of about 1260° C. and was maintained at such temperature for four hours. Controlled cooling at the rate of 1 to 5° C. per hour from the maximum of 1260° C. was then commenced by controlled energization of the furnace. This program was continued until approximately 975° C. At this point, the crucible was removed from the furnace and the still liquid portion poured off. After pouring off the liquid the crystals still in the crucible were permitted to cool. This is tantamount to an air quench, cooling taking of the order of one hour to reach the ambient temperature.

The crucible was then immersed in a vessel containing a dilute solution of nitric acid and water of the order of 30 percent by volume. The acid cleaning procedure was continued until all flux residue has been removed from the crystals. Under ordinary circumstances, acid cleaning at room temperature takes of the order of four hours, although this is variable, being dependent on the amount of residue, size of the charge, and number of clusters. It is found expeditious to carry out the acid cleaning at temperatures approximating 80° C. Subsequent to this, the acid solution was poured off, the crucible removed from the container, and the crystals washed in water. Following the washing step, the crystals were dried by air drying at room temperature. The resultant crystals were chemically analyzed and magnetic measurements were 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,

Table I

Example	Starting Ingredients (grams)		Flux Composition (grams)		Product
			BaO	B_2O_3	
1	Stoichiometric System:				
	Fe_2O_3	4.6	14.4	4.0	Yttrium iron garnet ($Y_3Fe_5O_{12}$).
	Y_2O_3	4.3			
2	Fe_2O_3	31.5	84.6	24.0	Do.
	Y_2O_3	20.5			
	(27% excess Fe^{+++})				
3	GaO	6.75	7.25	1.7	Yttrium gallium garnet ($Y_3Ga_5O_{12}$).
	Y_2O_3	4.25			

As will be evident to those skilled in the art, many variations and modifications can be practiced within the spirit and scope of the disclosure and claims to this invention.

What is claimed is:

1. The method of growing single crystals of the garnet structure consisting essentially of a compound represented by the formula $M_3Me_5O_{12}$ where M is at least one member selected from the group consisting of yttrium and rare earth elements having an atomic number within the range of 62 to 71, Me is at least one trivalent metal selected from the group consisting of trivalent iron, gallium, scandium, chromium and cobalt, and O is oxygen which comprises heating a nutrient consisting essentially of the constituent components of said garnet in stoichiometric amounts additionally containing up to 90 percent excess iron by weight when the trivalent matter selected is iron to a temperature of about 1260° C. together with a flux consisting essentially of a mixture of barium oxide and boron oxide, the weight ratio of barium oxide to boron oxide being in the range of 3.16:1 to 4.55:1, the gross nutrient to flux ratio being in the range of 1:1.8 to 1:4.5 by weight and cooling the resultant melt whereby said garnet precipitates from the melt in crystals.

2. The method of claim 1 in which said melt comprises Y_2O_3, Fe_2O_3, BaO and B_2O_3.

3. The method of claim 1 in which said melt comprises Y_2O_3, Ga_2O_3, BaO and B_2O_3.

4. The method of claim 1 wherein crystallization occurs over the range of 1255–990° C.

5. The method of claim 1 in which the weight ratio of BaO to B_2O_3 is 3.54:1.

6. The method of claim 1 wherein 27 percent excess Fe_2O_3 by weight in solution is employed.

References Cited in the file of this patent

UNITED STATES PATENTS

2,957,827 Nielsen ---------- Oct. 25, 1960