

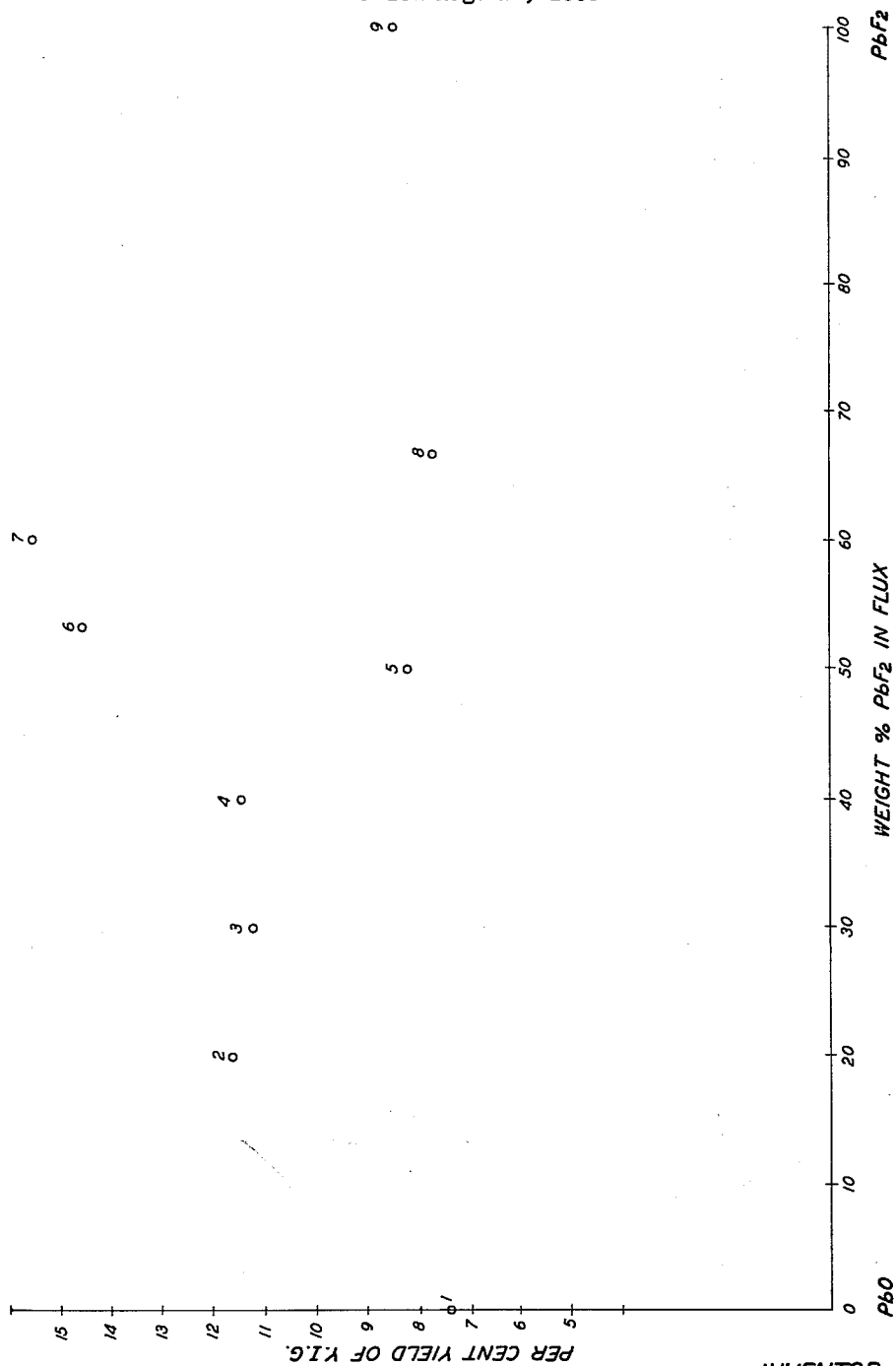
Aug. 21, 1962

J. W. NIELSEN

3,050,407

SINGLE CRYSTAL GARNETS

Filed Aug. 25, 1959



INVENTOR
J.W. NIELSEN
BY
George S. Lindig
ATTORNEY

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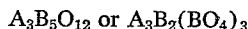
James W. Nielsen, Berkeley Heights, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

Filed Aug. 25, 1959, Ser. No. 836,008

7 Claims. (Cl. 106-42)

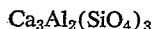
This invention relates to a method of growing single crystals of synthetic garnets in a flux comprising lead oxide and lead fluoride, and also to the garnet crystals so produced.

The synthetic garnet materials of particular interest can be represented by the formulas



where O is oxygen, and A and B are trivalent metals.

In particular, A may be yttrium or one of the rare earth elements of atomic number between 62 and 71, or mixtures of rare earth elements of atomic number between 57 and 71 with each other or with yttrium. B may be a trivalent metallic ion such as iron, gallium, aluminum or scandium, or mixtures thereof with each other or other metallic ions. Where A is yttrium and B is iron, the garnets are known as "yttrium-iron garnets." The synthetic materials described are termed "garnets," because they have the same complicated cubic structure as the mineral garnets, such as, for example, grossularite,



The synthetic garnets containing a substantial iron content are ferrimagnetic and can be used in the construction of inductive devices as cores therefor. Such garnets show the property 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 in the garnets is larger than in most other transparent materials, making them especially useful.

As is well known in the art, single crystals of ferrimagnetic material have certain magnetic properties not exhibited by the material in polycrystalline form. 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 applications Serial No. 778,352, filed December 5, 1958, now Patent No. 3,016,495 and Serial No. 774,172, filed November 17, 1958, now Patent No. 3,013,229. A convenient prior art method of 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 the molten bath by standard crystallization procedures. This technique is discussed in detail in copending application Serial No. 655,995, filed April 30, 1957, now U.S. Patent 2,957,827.

The present invention embodies the same general procedures as the aforementioned crystal growing method with the exception of the flux employed. The present inventive method utilizes a flux initially comprising lead fluoride or mixtures thereof with lead oxide. The use of such a flux is advantageous in several respects.

An important advantage, from an economic viewpoint, of the use of a flux comprising lead fluoride, is the substantial increase in the yield of single crystal garnets expressed in terms of yield per unit weight of melt. Thus, for example, in the production of yttrium-iron garnet single crystals, the use of a flux containing 20 percent by weight of lead fluoride and 80 percent by weight of lead oxide produced an amount of garnet which was approximately 50 percent greater than that resulting from the use of a flux consisting of 100 percent lead oxide.

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The quality and size of the garnet crystals produced by the present inventive method are both improved over those produced by the prior art method. Although the largest single crystals of yttrium-iron garnet produced in accordance with the prior art method were of the order of 2 grams, crystals as large as 20 grams have been produced by the present method. In addition, the number and size of inclusions in the crystals are substantially reduced.

As discussed more fully below, the addition of lead fluoride to the prior art flux simplifies the separation problem in the instances where the garnet crystals being produced are magnetic. Thus, for example, in the production of yttrium-iron garnet by the prior art process, crystals of magnetoplumbite ($PbFe_{12}O_{19}$) are formed along with the primary product. This necessitates magnetic separation of the crystal at different temperatures to take advantage of the different Curie points of the two magnetic materials. The addition of lead fluoride to the flux makes possible the adjustment of the proportions of the reactants so that the formation of magnetoplumbite is avoided while maintaining the yield of the desired garnet at substantially high levels.

An important general advantage of the use of a flux containing lead oxide and lead fluoride for the production of rare earth single crystal garnets inheres in the fact that the growing process may be conducted at lower temperatures than heretofore possible without sacrificing the yield. The solubility of the reactants in the flux increases at higher temperatures and, accordingly, the yield of single crystal garnets also increases with temperature. A practical limitation on the maximum temperature of the process is approximately 1400°C. , since above this temperature the melts very actively attack the platinum crucibles in which they are prepared. Since other materials commonly used in crucible manufacture, such as ceramics, are attacked even more readily than is platinum, no evasion of this practical limitation as yet appears feasible. Heretofore, production of rare earth garnet crystals using pure lead oxide as the flux was generally conducted at temperatures as close to 1400°C. as practicable in order to increase the solubility of the rare earth oxide reactants to the highest possible level. This resulted in substantial deterioration of the platinum crucibles. The addition of lead fluoride to the prior art flux substantially increases the solvent power of the flux with respect to the rare earth oxide reactants. The increase in solubility is sufficiently great to permit a decrease in the maximum temperature of the process and still maintain a yield advantage over the prior art process.

The inventive flux is especially suitable for the production of a new series of synthetic gems based on the yttrium-gallium garnet structure. The color of these gems is controlled by adding small amounts of certain metallic ions, such as chromium, to the melt.

The invention will be more readily understood when taken in conjunction with the drawing which depicts the percent yield of yttrium-iron garnet, calculated by dividing the weight of garnet produced by the total weight of the melt, as a function of the initial composition of the lead oxide-lead fluoride flux. The numbered points represent data obtained as described below.

A suitable procedure to be followed in the practice of this invention is outlined below.

The reactants are weighed, mixed together, and placed in a platinum crucible which is subsequently covered. The cover preferably is crimped on to the crucible to avoid evaporation of the contents. The crucible is then placed in a muffle furnace in which an oxygen-enriched atmosphere is maintained. The maintenance of an oxygen-enriched atmosphere decreases the tendency of molten lead oxide to reduce and attack the platinum crucible.

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The crucible is then heated to fuse the flux and thereby permit solution of the reactants. Heating at an elevated temperature is continued until a substantially homogeneous melt is produced. At temperatures of the order of 1250° C., heating periods are typically in the range of from one to twenty-four hours. The use of higher temperatures permits shorter heating times.

After fusion is complete, the melts are permitted to cool at a slow rate. Since equilibrium cooling is preferred, cooling should be as slow as possible. In general, cooling rates in the range of from 1° C. per hour to 10° C. per hour are advantageous although rates as high as 20° C. per hour may be used. After the crucible is cooled to a temperature preferably below 1050° C., to assure high yields, it is removed from the furnace and allowed to cool to room temperature. The solidified matrix is dissolved in a solvent such as a mixture of dilute nitric and acetic acids leaving the crystalline garnets unaffected.

The data shown in the drawing are presented to indicate the substantial increase in yield of garnet single crystals which is made possible by use of the inventive flux. Although the data relate to yttrium-iron garnet, it is to be understood that the advantages shown extend to the production of all garnet structures which require the use of a rare earth oxide as a starting material. In the prior art production of such garnet structures, a limiting factor with respect to yield was the low solubility of the rare earth oxide reactant in the lead oxide flux. In the present processes the addition of lead fluoride substantially increases the solubility of the rare earth oxides and thereby facilitates substantial increase in the yield.

In the drawing, point 1 represents the maximum percent yield of yttrium-iron garnet which has been produced in accordance with the prior art process using a flux of pure lead oxide. Under the conditions used to obtain the data exemplified by point 1, the melt was saturated with respect to yttrium oxide. The data with respect to point 1 were obtained as follows:

Example 1

A mixture consisting of 7 grams Y_2O_3 , 70 grams Fe_2O_3 , and 100 grams of PbO was heated to a temperature of 1350° C. for a period of 5 hours and then cooled at a rate of approximately 5° C. per hour to a temperature of 970° C. The yield of yttrium-iron garnet was determined to be 12.9 grams, thus the percent yield is equal to 12.9 divided by 177, or approximately 7.4 percent. Also formed were approximately 30 grams of magnetoplumbite.

Each of points 2 through 9 represents a production run in which yttrium-iron garnet was crystallized in a flux containing lead fluoride. The conditions under which the data for points 2 through 9 were obtained is set forth below, the number of the example corresponding to the number of the point. It is to be noted that in all instances the maximum temperature was less than 1350° C., the temperature used in Example 1. Also, the temperatures to which the melts were equilibrium cooled were greater than 970° C. which was the temperature employed in Example 1. It is to be understood that such conditions eliminated temperature as a factor in comparing yields at different flux compositions.

Example 2

A mixture consisting of 9 grams Y_2O_3 , 50 grams Fe_2O_3 , 20 grams PbF_2 , and 80 grams of PbO was heated in a covered platinum crucible to a temperature of 1325° C. in an oxygen-enriched atmosphere for a period of 5 hours and then cooled at a rate of approximately 5° C. per hour to a temperature of 1010° C. The yield of yttrium-iron garnet was determined to be 18.6 grams, and the percent yield is equal to 18.6 divided by 159, or 11.7 percent. Also formed were approximately 22.3 grams of magnetoplumbite.

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Example 3

A mixture consisting of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , 45 grams PbF_2 , and 105 grams of PbO was heated in a covered platinum crucible to a temperature of 1250° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 20° C. per hour to a temperature of 990° C. The yield of yttrium-iron garnet was determined to be 22.5 grams, and the percent yield is equal to 22.5 divided by 200, or 11.2 percent. No magnetoplumbite was formed.

Example 4

A mixture consisting of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , 60 grams PbF_2 , and 90 grams of PbO was heated in a covered platinum crucible to a temperature of 1250° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 2.3° C. per hour to a temperature of 1000° C. The yield of yttrium-iron garnet was determined to be 23.1 grams, and the percent yield is equal to 23.1 divided by 200, or 11.5 percent. No magnetoplumbite was formed.

Example 5

A mixture consisting of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , 75 grams PbF_2 , and 75 grams of PbO was heated in a covered platinum crucible to a temperature of 1250° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 20° C. per hour to a temperature of 1000° C. The yield of yttrium-iron garnet was determined to be 16.6 grams, and the percent yield is equal to 16.6 divided by 200, or 8.3 percent. No magnetoplumbite was formed.

Example 6

A mixture consisting of 30 grams Y_2O_3 , 45 grams Fe_2O_3 , 80 grams PbF_2 , and 70 grams of PbO was heated in a covered platinum crucible to a temperature of 1300° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 20° C. per hour to a temperature of 1000° C. The yield of yttrium-iron garnet was determined to be 32.8 grams, and the percent yield is equal to 32.8 divided by 200, or 16.4 percent. Also formed were approximately 5.8 grams of magnetoplumbite.

Example 7

A mixture consisting of 30 grams Y_2O_3 , 45 grams Fe_2O_3 , 90 grams PbF_2 , and 60 grams of PbO was heated in a covered platinum crucible to a temperature of 1300° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 20° C. per hour to a temperature of 1000° C. The yield of yttrium-iron garnet was determined to be 34.4 grams, and the percent yield is equal to 34.4 divided by 200, or 17.2 percent. Also formed were approximately 7.2 grams of magnetoplumbite.

Example 8

A mixture consisting of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , 100 grams PbF_2 , and 50 grams of PbO was heated in a covered platinum crucible to a temperature of 1250° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 2.3° C. per hour to a temperature of 1000° C. The yield of yttrium-iron garnet was determined to be 15.7 grams, and the percent yield is equal to 15.7 divided by 200, or 7.8 percent. Also formed were approximately 7.5 grams of magnetoplumbite.

Example 9

A mixture consisting of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , and 150 grams PbF_2 was heated in a covered platinum crucible to a temperature of 1250° C. in an oxygen-enriched atmosphere for a period of 4 hours and then cooled at a rate of approximately 2.3° C. per hour to a temperature of 1000° C. The yield of yttrium-iron

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garnet was determined to be 17.2 grams, thus the percent yield is equal to 17.2 divided by 200, or 8.6 percent. Also formed were approximately 12.1 grams of magnetoplumbite.

As can be seen from the drawing, each of points 2 through 9 represent percent yields which are greater than that of point 1. The yields represented by points 6 and 7 are approximately twice that of point 1.

It is believed that Example 9, the yield of which is plotted as point 9 in the drawing, should be discussed more fully. Although the flux used was initially 100 percent lead fluoride, it has been determined that substantial amounts of lead fluoride were converted to lead oxide in the course of the run. It is believed that such conversion results from interaction of the oxygen in the atmosphere with the lead fluoride flux. Accordingly, within a very short period of time following the inception of a production run, a flux which may have initially been pure lead fluoride is converted to a mixture of lead oxide and lead fluoride.

Experimental data has also indicated that the yields of garnet are higher at lower cooling rates. Thus, for example, increasing the cooling rate of Example 4 to 20° C. per hour results in a decrease in yield of approximately 25 percent. The yield of Example 5, which appears as a discontinuity in the drawing, would be approximately equal to that of Example 4 if the cooling rate were commensurately reduced. Accordingly, in those areas where the yield tends to be low, as, for example, at flux concentrations of greater than 80 percent PbF_2 , a cooling rate of less than 5° C. per hour is preferred.

As stated above, one of the advantages of the use of the flux of this invention is the elimination of magnetoplumbite as a by-product in the production of yttrium-iron garnet. It is noted that in Examples 3, 4 and 5 above, no magnetoplumbite was formed. At lead fluoride concentrations greater than those employed in Examples 3, 4 and 5 the formation of magnetoplumbite may be avoided by adjusting the ratio of yttrium oxide to iron oxide in the melt so as to shift position on the phase diagram to a more desirable point. This was accomplished in the instance of Example 10 set forth below.

Example 10

A mixture consisting of 22 grams Y_2O_3 , 30 grams Fe_2O_3 , 90 grams PbF_2 , and 60 grams PbO was heated to a temperature of approximately 1300° C. for a period of 4 hours and then cooled at a rate of approximately 20° C. per hour to a temperature of 1005° C. The yield of yttrium-iron garnet was found to be 17 grams, and the percent yield was equal to 8.4 percent. No magnetoplumbite was formed.

A comparison of Example 10 with Example 7 indicates that a sacrifice in yield was necessary in order to eliminate the presence of magnetoplumbite. However, the reduced yield of Example 10 is still greater than that of Example 1, and the elimination of a separation step may compensate for the decrease in yield.

Deterioration of platinum crucibles is substantially lessened by use of the inventive flux. Such beneficial effect results directly from the lower temperatures made possible by the addition of lead fluoride to the prior art lead oxide flux. Operations may be conducted at these lower temperatures by reason of the increased solubility of the reactants in the lead fluoride flux. Thus, for example, the reactants used in Example 1 above may be dissolved in an equal weight of flux containing 5 percent lead fluoride at a temperature approximately 50° C. lower than that which would be required if the flux were pure lead oxide. Such a decrease in temperature substantially lessens the severity of attack of the platinum crucibles commonly used.

A substantial increase in the size of single crystal garnets is made possible by the use of the inventive flux. For

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instance, several single crystals of yttrium-iron garnet of the order of 18 grams in weight were produced as described in Example 11, below. It is noted that a run different from that of Example 11 only in that the flux was pure lead oxide resulted in crystals which were no larger than 3 grams.

Example 11

A mixture of 250 grams Y_2O_3 , 375 grams Fe_2O_3 , 800 grams PbO , and 1000 grams PbF_2 was introduced into a cylindrical platinum crucible approximately 4 inches in height and 4 inches in diameter. The crucible was covered and was placed into a flux in which an oxygen-enriched atmosphere was maintained. The crucible and contents were heated to a temperature of approximately 1260° C. and maintained at that temperature for approximately 20 hours. The crucible and contents were then cooled at a rate of approximately ½° C. per hour to a temperature of approximately 1000° C. A temperature gradient of approximately 10° C. was maintained between the top and bottom of the crucible, the top being maintained at the higher temperature.

The molten flux was decanted from the crucible, and the crucible and contents then cooled to room temperature. The contents were then leached with a mixture of dilute nitric and acetic acids to dissolve the remaining flux. The largest single crystal produced was approximately 19 grams in weight. Several single crystals of the order of 18 grams in weight also resulted.

The lead oxide-lead fluoride flux of this invention may also be employed for the production of single crystal garnets embodying elements other than yttrium, and also embodying yttrium in combination with such other elements. Garnets may be produced in which yttrium is used in combination with rare earth elements of atomic number 57 through 71. Single crystal garnets embodying rare earth elements 62 through 71 or combinations thereof may also be produced. Listed below are several examples of the production of such single crystal garnets.

Example 12

A mixture of 12 grams of terbium oxide (Tb_2O_3), 30 grams Fe_2O_3 , 80 grams of PbF_2 and 70 grams PbO was heated in a covered platinum crucible at a temperature of 1250° C. for 4 hours in an oxygen-enriched atmosphere. The crucible was cooled at a rate of 1° C. per hour to a temperature of 975° C., and was then air-cooled to room temperature. Single crystals of $\text{Tb}_3\text{Fe}_5\text{O}_{12}$ resulted.

Example 13

A mixture of 25 grams of erbium oxide (Er_2O_3), 60 grams Fe_2O_3 , 60 grams of PbF_2 and 90 grams PbO was heated in a covered platinum crucible at a temperature of 1300° C. for 5 hours in an oxygen-enriched atmosphere. The crucible was cooled at a rate of 1° C. per hour to a temperature of 890° C., and was then air-cooled to room temperature. Single crystals of $\text{Er}_3\text{Fe}_5\text{O}_{12}$ resulted.

Example 14

A mixture of 25 grams of ytterbium oxide (Yb_2O_3), 60 grams Fe_2O_3 , 60 grams of PbF_2 and 90 grams PbO was heated in a covered platinum crucible at a temperature of 1300° C. for 5 hours in an oxygen-enriched atmosphere. The crucible was cooled at a rate of 1° C. per hour to a temperature of 890° C., and was then air-cooled to room temperature. Single crystals of $\text{Yb}_3\text{Fe}_5\text{O}_{12}$ resulted.

Example 15

A mixture of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , 0.36 grams gadolinium oxide (Gd_2O_3), 90 grams of PbF_2 and 60 grams PbO was heated in a covered platinum crucible at a temperature of 1260° C. for 8 hours in an oxygen-enriched atmosphere. The crucible was cooled at a rate of 1° C. per hour to a temperature of 930° C., and was

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then air-cooled to room temperature. Single crystals of $(Y_{.99}Gd_{.01})_3Fe_5O_{12}$ resulted.

Example 16

A mixture of 20 grams Y_2O_3 , 30 grams Fe_2O_3 , 0.063 grams holmium oxide (Ho_2O_3), 90 grams of PbF_2 and 60 grams PbO was heated in a covered platinum crucible at a temperature of $1250^\circ C$. for 4 hours in an oxygen-enriched atmosphere. The crucible was cooled at a rate of $1^\circ C$. per hour to a temperature of $985^\circ C$., and was then air-cooled to room temperature. Single crystals of $(Y_{.99}Ho_{.01})_3Fe_5O_{12}$ resulted.

The inventive flux is also suitable for producing substituted yttrium-iron garnets of the type described in an article by M. Gillo and S. Geller in the Physical Review, volume 110, page 73. In such garnets a trivalent ion, such as scandium, aluminum, indium, gallium, or chromium, is substituted for iron in the crystal lattice. An example of the production of such a substituted garnet is described below.

Example 17

A mixture of 20 grams Y_2O_3 , 26.25 grams Fe_2O_3 , 3.25 grams Sc_2O_3 , 90 grams PbF_2 , and 60 grams PbO was heated to a temperature of approximately $1260^\circ C$. for a period of 8 hours and then cooled at a rate of approximately $1^\circ C$. per hour to a temperature of $930^\circ C$. Single crystals of scandium substituted yttrium-iron garnet resulted.

A new series of synthetic gemstones have been produced using the flux of the present invention. These new gemstones are based on yttrium-gallium garnet ($Y_3Ga_5O_{12}$). Single crystals of yttrium-gallium garnet are colorless, transparent, and possess a refractive index of approximately 1.82, and a hardness of between 7 and 8 on the Moh scale. The addition of small quantities of any of several metallic oxides imparts an attractive color to the garnet crystals. Thus, for example, the addition of chromium to this garnet produces a green gemstone, the addition of cobalt produces a blue-green stone, and the addition of manganese produces a stone having a ruby coloration. The gemstones exhibit refractive indices as high as 1.85, depending upon the depth of color of the particular stone. The hardness of the stones compares favorably with amethyst, and has a value of between 7 to 8 on the Moh hardness scale. Examples of the variety of gemstones, in addition to pure yttrium-gallium garnet, which may be produced in accordance with this invention are set forth in detail below.

Example 18

A mixture consisting of 24 grams Y_2O_3 , 48 grams Ga_2O_3 , 180 grams PbF_2 , 160 grams PbO , and 2.5 grams Cr_2O_3 was introduced into a platinum crucible which was then covered and placed into a furnace in which an oxygen-enriched atmosphere was maintained. The crucible and contents were heated to a temperature of $1250^\circ C$. and maintained at that temperature for approximately four hours. The crucible and contents were then cooled at a rate of approximately $1^\circ C$. per hour to a temperature of approximately $950^\circ C$. The crucible was then allowed to cool to room temperature. The contents were then leached with a mixture of dilute nitric and acetic acids to dissolve the flux and recover the garnet crystals. The gemstones were green in color.

Example 19

The procedure of Example 11 was followed with the exception that 0.16 gram of Co_3O_4 as added in place of 2.5 grams of Cr_2O_3 . The garnet crystals so formed were blue-green in color.

Example 20

The procedure followed was similar to that of Example 11 with the exception that 0.16 gram Co_3O_4 and 4 grams

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TiO_2 was added in place of 2.5 grams of Cr_2O_3 . The garnet crystals produced were teal-blue in color.

Example 21

The procedure followed was similar to that of Example 11 with the exception that 0.25 gram Mn_2O_3 was added in place of 2.5 grams of Cr_2O_3 . The garnet crystals produced were ruby in color.

Example 22

The procedure followed was similar to that of Example 11 with the exception that 0.125 gram NiO was added in place of 2.5 grams of Cr_2O_3 . The garnet crystals produced were chartreuse in color.

Example 23

The procedure followed was similar to that of Example 11 with the exception that 0.1 gram Fe_2O_3 and 0.5 gram Co_3O_4 was added in place of 2.5 grams of Cr_2O_3 . The garnet crystals produced were emerald-green in color.

Excessive addition of the certain metallic oxides may cause the garnet crystals to become opaque, thereby depriving them of their gem-like qualities. In the instance of other metallic oxides the maximum amounts which may be added are determined by other considerations. Listed in tabular form below are the minimum and maximum limits of the additives, shown in Examples 18 through 23 above, to yield a garnet having gem-like properties. The minimum and maximum limits are expressed as a percentage computed by dividing the number of mols of additive by the sum of the mols of additive plus mols of gallium oxide in the melt.

Table I

Additive	Minimum, percent	Maximum, percent
Cr_2O_3	.1	12
Co_3O_4	.001	2
TiO_2	.1	10
Mn_2O_3	.01	3
NiO	.01	.1
Fe_2O_3	.01	1

The minimum limit for each of the additives of Table I is occasioned by the fact that substantially smaller quantities do not produce a readily apparent color change.

The maximum limits in the instances of Mn_2O_3 and Co_3O_4 are determined by the fact that substantially larger quantities cause the crystals to become opaque.

The maximum quoted for Cr_2O_3 may be exceeded without affecting the gem-like qualities of the crystal. However, it has been determined that a new phase or compound is formed between the Cr_2O_3 in excess of 12 percent and another ingredient of the melt. Accordingly, additions of Cr_2O_3 in excess of 12 percent may result in a decrease of the total amount of yttrium-gallium garnet formed but have no effect on the coloration or appearance thereof.

The maximum limit in the instance of NiO represents the approximate upper limit of the solubility of NiO in the melt.

In the instances of Fe_2O_3 and TiO_2 the maximum figures quoted represent a practical upper limit in that additions in excess of these quantities do not appreciably enhance the attractiveness of the garnet crystals.

It is to be appreciated that the examples set forth above are intended merely as illustrative of the advantages to be gained by the use of the flux of this invention. The number and variety of single crystal materials which may be produced are infinite. Variations may be made by one skilled in the art without departing from the spirit and scope of this invention.

What is claimed is:

1. The method of producing single crystals of the gar-

net structure comprising a compound represented by the formula



where

A is at least one element selected from the group consisting of yttrium and the rare earth elements of atomic number between 57 and 71 inclusive,

B is at least one metal selected from the group consisting of iron, aluminum, scandium, indium, gallium and chromium and

O is oxygen,

comprising the steps of forming a melt consisting essentially of A, B, PbF_2 , together with lead oxide, the latter in an amount of from 0 to 400 weight percent based on the amount of PbF_2 present, and cooling the melt to produce single crystals.

2. The method of claim 1 in which A is yttrium, and in which the said melt consists essentially of Y_2O_3 , PbO , PbF_2 , and at least one oxide selected from the group consisting of Fe_2O_3 , Al_2O_3 , Sc_2O_3 , In_2O_3 , Ga_2O_3 , and Cr_2O_3 .

3. The method of claim 1 in which

A is yttrium,

B is iron,

and in which the melt consists essentially of Y_2O_3 , PbO , PbF_2 , and Fe_2O_3 .

4. The method of claim 3 in which the weight ratio of PbO to PbF_2 in the melt is in the approximate range of from 7:3 to 2:3.

5. The method of claim 3 in which the weight ratio of Fe_2O_3 to Y_2O_3 is approximately 3:2 and the weight ratio of PbF_2 to PbO is approximately 5:4.

6. The method of claim 1 in which

A is yttrium,

B is gallium,

and in which the melt consists essentially of Y_2O_3 , Ga_2O_3 , PbO , and PbF_2 .

7. The method of growing single crystal gems of the garnet structure comprising the steps of forming a melt consisting essentially of Y_2O_3 , Ga_2O_3 , PbO , PbF_2 , said PbO being present in an amount of from 0 to 400 weight percent based on the amount of PbF_2 present, and at least one oxide selected from the group consisting of Cr_2O_3 , Co_3O_4 , TiO_2 , Mn_2O_3 , NiO , and Fe_2O_3 , and cooling the melt to produce single crystals.

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