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3,091,540

GARNET GEMSTONES

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This application is a division of copending application Serial No. 836,008, filed August 25, 1959, now U.S. Patent 3,050,407.

This invention relates to a novel series of synthetic gems based on the yttrium-gallium garnet structure.

Single crystals of yttrium-gallium garnet ($Y_3Ga_5O_{12}$) are colorless, transparent, and typically possess a refractive index of approximately 1.82, and a hardness of between 7 and 8 on the Mohs' 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. These 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 Mohs' hardness scale. Examples of the variety of gemstones which may be produced in accordance with this invention are set forth in detail below.

The synthetic gemstones disclosed herein are prepared from a flux initially comprising lead fluoride or mixtures thereof with lead oxide. The use of such a flux is advantageous in several respects, the most important being the high yields of single crystal garnets expressed in terms of yield per unit weight of melt.

An important general advantage of the use of a flux containing lead oxide and lead fluoride for the production of yttrium gallium garnets inheres in the fact that the growing process may be conducted at lower temperatures than are generally employed in crystal growing processes without sacrificing the yield. The solubility of the reactants in the flux increases at higher temperatures and, accordingly, the yield of single crystal garnet also increases with temperature. A practical limitation on the maximum temperature of the process is approximately 1400° C., since above this temperature the melts 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. 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 is preferably crimped onto the crucible in order 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.

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

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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 lead oxide-lead fluoride flux is employed such that lead oxide is present in an amount of from 0 to 400 weight percent based on the amount of lead fluoride present. Thus, the weight ratio of PbO to PbF₂ is in the approximate range of 4:1 to 0.

The following examples are given by way of illustration and are not to be construed as limiting the invention, many variations of which are possible within the spirit and scope thereof.

EXAMPLE 1

A mixture consisting of 24 grams Y₂O₃, 48 grams Ga₂O₃, 180 grams PbF₂, 160 grams PbO, and 2.5 grams Cr₂O₃ 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° C. and maintained at that temperature for approximately four hours. The crucible and contents were then cooled at a rate of approximately 1° C. per hour to a temperature of approximately 950° 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 2

The procedure of Example 1 was followed with the exception that 0.16 gram of Co₃O₄ was added in place of 2.5 grams of Cr₂O₃. The garnet crystals so formed were blue-green in color.

EXAMPLE 3

The procedure of Example 1 was repeated with the exception that 0.16 gram of Co₃O₄ and 4 grams TiO₂ were added in place of 2.5 grams of Cr₂O₃. The garnet crystals produced were teal blue in color.

EXAMPLE 4

The procedure of Example 1 was repeated with the exception that 0.25 gram Mn₂O₃ was added in place of 2.5 grams of Cr₂O₃. The garnet crystals produced were ruby in color.

EXAMPLE 5

The procedure of Example 1 was repeated with the exception that 0.125 gram of NiO was added in place of 2.5 grams of Cr₂O₃. The garnet crystals produced were chartreuse in color.

EXAMPLE 6

The procedure of Example 1 was repeated with the exception that 0.1 gram Fe₂O₃ and 0.5 gram Co₃O₄ was added in place of 2.5 grams of Cr₂O₃. The garnet crystals produced were emerald green in color.

Excessive addition of 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 1-6 above, to yield a garnet having gem-like properties. The minimum and maximum limits are expressed as a percentage computed

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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

Additive	Minimum, percent	Maximum, percent
Cr ₂ O ₃ -----	0.10	12
Co ₃ O ₄ -----	0.001	2
TiO ₂ -----	0.10	10
Mn ₂ O ₃ -----	0.01	3
NiO-----	0.01	0.1
Fe ₂ O ₃ -----	0.01	1

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

The maximum limits in the instances of Mn₂O₃ and Co₃O₄ are determined by the fact that substantially larger quantities cause the crystals to become opaque.

The maximum quoted for Cr₂O₃ 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 Cr₂O₃ in excess of 12 percent and another ingredient of the melt. Accordingly, additions of Cr₂O₃ 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 Fe₂O₃ and TiO₂ 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 will be appreciated that the examples set forth above are intended merely as illustrative of the advantages to be gained by the use of the PbO—PbF₂ flux. 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. A single crystal gem of the garnet structure consist-

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ing essentially of a compound represented by the formula Y₃Ga₅O₁₂ and at least one additive selected from the group consisting of Cr₂O₃, Co₃O₄, mixtures of TiO₂ and Co₃O₄, Mn₂O₃, NiO and mixtures of Fe₂O₃ and Co₃O₄, said additive being present in an amount within the following range

	Percent
Cr ₂ O ₃ -----	0.10-12
Co ₃ O ₄ -----	0.001-2
TiO ₂ -----	0.10-10
Mn ₂ O ₃ -----	0.01-3
NiO-----	0.01-0.1
Fe ₂ O ₃ -----	0.01-1

the said percentage being the ratio of the number of mols of additive to the sum of the number of mols of additive and gallium oxide employed in preparing the said crystal.

2. A single crystal gem in accordance with claim 1 wherein said additive is Cr₂O₃.

3. A single crystal gem in accordance with claim 1 wherein said additive is Co₃O₄.

4. A single crystal gem in accordance with claim 1 wherein said additive consists of a mixture of Co₃O₄ and Fe₂O₃.

5. A single crystal gem in accordance with claim 1 wherein said additive is Mn₂O₃.

6. A single crystal gem in accordance with claim 1 wherein said additive consists of a mixture of Co₃O₄ and TiO₂.

7. A single crystal gem in accordance with claim 1 wherein said additive is NiO.

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