

[54] SYNTHETIC CRYSTAL AND METHOD OF MAKING SAME

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[57] ABSTRACT

An improved synthetic gem-like crystal simulating alexandrite and method of making the same, wherein, in one embodiment, the crystal is grown on a chrysoberyl seed placed in a flux melt environment with the flux melt including a flux material, a nutrient material and suitable dopants to provide color changes to the crystal which simulates alexandrite in daylight and tungsten light. A typical flux material is lithium polymolybdate, the nutrient material is typically aluminum oxide and beryllium oxide, and the dopants include iron and chromium. In another embodiment, the crystal is grown by using the Czochralski method, wherein a nutrient and suitable dopants including iron and chromium are heated to form a melt. A seed is pulled from the melt at a predetermined rate, during which time growth occurs on the seed. The crystal can also be formed by using the Bridgman, Verneuil and floating zone methods. The iron and chromium in the dopants are in predetermined concentrations to achieve the aforesaid color changes in the crystals formed by the methods.

11 Claims, No Drawings

SYNTHETIC CRYSTAL AND METHOD OF MAKING SAME

BACKGROUND OF THE INVENTION

The compound, alexandrite, so named after the Russian Czar Alexander, is a colored variety of the mineral chrysoberyl $\text{BeO} \cdot \text{Al}_2\text{O}_3$. It is found naturally in a variety of locations throughout the world but only in very limited quantities. The most precious stones are said to come from the Ural Mountain region of Russia. The exact chemical composition of alexandrite varies with the locale in which it is found; hence, there is great difficulty generally in assigning a specific coloring composition to the host material which is chrysoberyl.

Several references relating to alexandrite indicate that chromium is the coloring agent responsible for the color change that occurs when alexandrite crystals are exposed to light of different wavelengths. One of such references is "The Alexandrite Effect: An Optical Study", American Mineralogist, Volume 52, Page 867 (1967). In these references it is stated that chromium causes remarkable pleochroism in alexandrite. The colors are yellow, green and red for light polarized along the *a*, *b* and *c* crystallographic axes, respectively, of the alexandrite crystal. An intense absorption in the dark blue region dominates the *a* axis spectrum, giving transmitted light its complementary color, yellow. Blue is again absorbed in the spectra of the *b* and *c* axes, but the transmitted colors are influenced by the absorption band near 0.6 microns wavelength. The latter absorbs yellow for the *c* axis and both red and yellow for the *b* axis. As a result, red is the dominant *c* axis color while only green radiation (0.5 microns wavelength) is transmitted for light polarized parallel to the *b* axis.

There have been indications in several other references that a variety of other elements are found in the natural alexandrite material, but to date, systematic attempts have been made but have been unsuccessful in obtaining the exact color characteristics of alexandrite which is one of the world's most prized gems. Attempts have been successful to produce the desired color change using a chromium dopant alone in very small crystals. However, in crystals of usable size, the green is lost if only chromium is used. Thus, as hereinafter described, iron is an essential ingredient in making gems of useful or commercial size having the proper color change characteristics. For purposes of this definition, a gem of useful or commercial size is a properly proportioned gem of 2 to 3 millimeters across the width thereof or larger.

SUMMARY OF THE INVENTION

The present invention is directed to a synthetic gem-like crystal and method of making the same, wherein the crystal has an orthorhombic configuration and simulates natural alexandrite with respect to color and composition. The method includes growing the crystal from a natural seed or a seed created from a natural seed. The method utilizes a flux melt technique from fluxes such as niobate (LiONb_2O_5), molybdate, tungstate (a salt or ester of tungstic acid) and lead-oxyfluoride. The fluxes are doped with a suitable material to give the appropriate color change to the crystal in daylight and tungsten light.

A preferred combination of such dopants includes iron oxide and chromium oxide in predetermined amounts. Tests have been made on the concentrations

and chemical nature of the impurities or dopants that must be added to the flux to give the desired color to the crystal. The dominance and respective intensities of these colors are very sensitive to the concentrations of chromium and iron in the finished crystal and the seed. To obtain the proper color change, the ratio of iron to chromium has to be adjusted according to the size of the cut gem which is desired. The result provides a crystal which simulates a high-quality gem having the color and composition of alexandrite yet the crystal is obtained at a cost must less than the cost of alexandrite in its natural form.

A detailed series of tests has shown that the best quality growth of crystals simulating alexandrite with the use of neither natural or created seeds is obtained by having growth faces of the following orientations: the 020 plane, the 031 plane, the 021 plane, the 222 plane and the 220 plane. The best quality growth appears to come from the 220, 020, and 021 planes. There does not appear to be significant difference in the growth kinetics between these several planes but there is a significant difference in the color change, depending upon the growth plane.

A considerable number of tests have been made on the concentrations and chemical natures of the impurities that must be added to the flux or the nutrient where flux is not used to give the desired color to the crystals. The dominance and respective intensities of these colors are very sensitive to the concentrations of chromium and iron in the finished crystal and the seed. In particular, the unique coloring of the gem alexandrite is completely masked if the chromium concentration exceeds 5% by weight in the finished crystal. The consequence of this is that the expected "green" daylight color is not exhibited and one sees with the eye only the strong red color independent of crystal orientation. This effect can be compensated for by controlled additions of an iron compound into the flux and/or nutrient. The chromium concentration effect is dominating, hence the desired gem colors are best obtained by the appropriate concentrations of chromium and iron in the ranges set forth hereinafter.

In accordance with the present invention, alexandrite can also be grown by another technique commonly referred to as the "Czochralski" technique. For a discussion of the essentials of this technique, reference is made to the article "Application of Czochralski Crystal-Pulling Technique to High-Melting Oxides," found in Journal American Ceramic Society 45, 474 (1962). In this technique, a melt is obtained by heating a mixture of a nutrient material and dopant materials including chromium and iron. The temperature reached by the melt is above the melting point of chrysoberyl. A seed is dropped into the melt and, at an appropriate time, pulling is initiated whereby the seed is progressively pulled from the melt at a predetermined rate. The crystal growth on the seed thus occurs and such growth can be separated from the seed at the completion of a growth cycle.

The primary object of this invention is to provide a synthetic crystal and method of making the same, wherein the crystal is of chrysoberyl having chromium and iron in sufficient quantity so that the crystal, although synthetic, resembles and thereby simulates natural alexandrite so as to permit the crystal to be used as a gem-like ornamentation in jewelry articles and the like.

Another object of this invention is to provide a synthetic crystal of the type described which results from the nucleation on seeds deposited in a mixture containing a nutrient and several dopants including iron and chromium so that the growth on the seeds can occur in a sequence to assure that the crystal will have the desired consistency and will provide the color changes in daylight and tungsten light appropriate to natural alexandrite itself.

A further object of this invention is to provide a method of forming a synthetic crystal of the type described, wherein the method includes the preparation of a mixture which includes a nutrient material and dopants in predetermined proportions by weight so that, when the mixture is subjected to high temperature and melted and when seeds have been deposited therein, the proper crystalline growth on the seeds will occur so as to result in a gem-like product containing the proportion of iron and chromium needed to produce the color change substantially corresponding to that of natural alexandrite.

Another object of this invention is to provide a method for forming a synthetic crystal of the aforesaid character, wherein the method can utilize a flux melt or can be of the Czochralski, Verneuil or Bridgman Techniques, wherein iron and chromium are used in combination to provide a crystal which gives color changes in daylight and tungsten light corresponding to that given by natural alexandrite.

A further object of this invention is to provide a composition of matter for use in carrying out the aforesaid method, wherein said composition includes a flux melt comprised of a flux material, a nutrient and several dopants, with the dopants containing iron in the range of about 0.07% to 3.0% by weight of the flux melt and chromium in the range of 0.0000685% to 0.5130% by weight of the flux melt, so that, when the composition is used in the process, the resulting crystal will have iron in the range of about 0.07% to 4.89% by weight of the crystal and chromium in the range of about 0.0342% to 2.05% by weight of the crystal to thereby provide the necessary crystalline structure and color to simulate natural alexandrite.

Other objects of this invention will become apparent as the following specification progresses.

A first method for carrying out the invention for making the synthetic crystal described above is comprised of a number of steps including combining a flux material with a nutrient material and with dopants to provide a mixture which is placed into a crucible or pot. The apparatus for carrying out the process includes a furnace of any suitable construction, such as the type having a cylindrical body and a hole in the bottom thereof through which the pot containing the mixture is elevated from beneath. An elevator is used to raise and lower the pot and to position the same within the furnace so that the mixture in the pot can be heated to a temperature of about 1200°C. At such temperatures, the mixture is in a flowable condition.

Preferably, the seed on which crystalline growth is to occur is lowered into the furnace from above. Thus, a suspension system above the furnace includes a support from which a platinum wire connected to the seed is suspended. Typically, there are a number of seeds used in carrying out the method. These seeds can be lowered into the pot and the present process contemplates the use of 118 seeds which are arranged in a single horizon-

tal row. It is possible to use a second row of 118 seeds above the first row, making a total of 236 crystals being grown simultaneously.

The seed is prepared by selecting a natural chrysoberyl crystal or synthetic material and orienting and sawing it if necessary. Then the seed is secured in some manner to a platinum wire and attached to the suspension system for lowering into the furnace. If desired, crystal growth following the teachings of the present invention can occur by spontaneous nucleation.

The mixture in the pot and the seeds are heated before the seeds are lowered into the fluidized flux mixture. The heating curve increases in positive slope until the desired temperature is reached. The temperature obtained is a characteristic of the furnace so that different furnaces will have different maximum operating temperatures. The movement of the seeds into the pot generally occurs when the temperature of the furnace has reached its maximum value; at that time, the seeds are lowered into the pot and the furnace is allowed to cool very slowly, such that the temperature of the mixture decreases progressively, typically about 1°C. per hour over typically a seven-day cycle. Thus, the period of crystal growth requires oftentimes seven to nine weeks.

The materials which comprise the mixture are typically as follows: the flux material is lithium polymolybdate ($\text{Li}_2\text{MoO}_4 \cdot 0.1\text{MoO}_3$ to $\text{Li}_2\text{MoO}_4 \cdot 4.0\text{MoO}_3$) which is more than 95% by weight of the entire material content of the pot. Next, there is the nutrient material which can be aluminum oxide and beryllium oxide, about 4% by weight of the entire material content of the pot. Finally, the mixture includes the dopants which, for purposes of illustration, include iron oxide and chromium oxide, which, collectively, might make up less than 2% by weight of the material content of the pot. The range of iron oxide in the flux melt is about 0.1% to 4.0% by weight thereof. To obtain the content of iron itself in the flux melt, this range is multiplied by a factor of about 0.7. Thus, the iron content in the flux melt is in the range of approximately 0.07% to 2.8% by weight of the flux melt.

The amount of chromium oxide in the flux melt is about 0.0001% to 0.5% by weight thereof. Using a multiplying factor of about 0.685 for the low end and 1.026 for the upper end, the amount of chromium in the flux melt with respect to the last-mentioned range is approximately 0.0000685% to 0.5130 by weight. The amount of nutrients chosen is set to obtain saturation of the nutrients in the overall flux content of the pot at the maximum temperature of the pot.

When the maximum temperature has been reached, the seeds are lowered into the pot and growth on the seeds commences to occur. The growth may continue until the temperature has lowered to about the freezing point of the flux. Then the seeds with the crystalline growth thereon are removed from the furnace and cut to separate the seeds from the crystals grown on the seeds. The resulting crystals have iron in the range of 0.07% to 4.89% by weight and chromium in the range of 0.0342% to 2.052% by weight. A crystal within this range of iron and chromium provides a high-quality gem-like product which gives the color change of natural alexandrite.

The conditions for melt crystal growth using this technique are met by alexandrite since the compound BeAl_2O_4 with its coloring elements is congruent melt-

ing, i.e., a substance that does not decompose to form other substances on melting. A number of other techniques can be used for congruent melting substances such as the Czochralski, Verneuil, floating zone and Bridgman and their variations. For a discussion of these techniques, reference is made to an article by M. Tanenbaum, "Single Crystal Growing", found in *Methods of Experimental Physics*, Vol. 6, Solid State Physics: Academic Press, N.Y., 1959, pp 86-121. Both the Verneuil or flame fusion and the floating zone methods are attractive but control of the growth parameters is more difficult; therefore, the Czochralski and Bridgman techniques are more preferred.

The most suitable crucible material for use in forming alexandrite is Iridium which does not react with the coloring agents (Cr, Fe) and can be used in oxidizing atmospheres. If no coloring agents were used, molybdenum or tungsten would be satisfactory.

In an experimental arrangement used to form alexandrite, a high frequency (450 KC) induction generator can be used to couple inductively with the Iridium crucible. The space around and below the crucible is filled with zirconia to provide thermal and electrical insulation. The zirconia is contained within a quartz envelope to prevent excessive oxidation of the Iridium since BeAl_2O_4 melts about 1870°C.

The respective oxides of BeO , Al_2O_3 , Cr_2O_3 and Fe_2O_3 are mixed in the proper proportions and pre-reacted to reduce the volume of the oxide powders. They are then placed into the crucible and heated over 1870°C. to obtain a melt. The temperature is monitored by optical pyrometers during the growth. The melt-down step may take several cycles in order to get a sufficient amount of material into the crucible.

Using any of the Czochralski, Verneuil, floating zone or Bridgman techniques, chromium oxide should be in the range of 0.05% to 2.5% by weight of the melt and the iron oxide should be in the range of 0.1% to 7.0% by weight of the melt. This would cause the chromium in the melt to be in the range of 0.03420% to 2.565% by weight of the melt and iron in the melt to be in the range of 0.0699% to 4.89% by weight of the melt. Using these ranges, the resulting crystal would have chromium in the range of about 0.0342% to 2.052% by weight of the crystal and iron in the range of about 0.07% to 4.89% by weight of the crystal.

A seed of BeAl_2O_4 either natural or synthetic is mounted to a rod of Al_2O_3 and fastened with Iridium wire. The seed rod is rotated about 60 rpm. When ready, the seed is dipped into the melt to initiate growth. At the appropriate time pulling is initiated. Pulling rates of 0.050-0.150 inches per hour have been found to be satisfactory. The seed orientation is not crucial but b axis is preferred for higher quality growth. When the growth has progressed to a sufficient length, the crystal is "burned in" to reduce the number of grains and then allowed to grow out to the desired diameter. This insures a high-quality crystal. The diameter of the growth crystal is held constant by elaborate control and the crystal is pulled to the desired length and finally "burned off." The grown crystal is then slowly cooled to prevent cracking from thermal shock. Crystals of over 1000 carats have been pulled by this method; such crystals have been strain- and core-free.

Example 1

In a particular example, 199 grams of pre-melted

BeAl_2O_4 (chrysoberyl), 0.12 grams Cr_2O_3 , and 0.24 grams Fe_2O_3 were added in a 2-inch diameter Iridium crucible, which was placed into a setup prepared for induction melting. A gas mixture containing nitrogen and oxygen was diffused into the quartz chamber. The crucible with its contents was heated to about 1950°C and held for one-half hour. The temperature was monitored by an optical pyrometer. A "b" axis seed crystal, which had been previously obtained from a melt of BeAl_2O_4 was dipped into the melt and growth was initiated.

The crystal was rotating at 60 rpm. At the appropriate time of outward growth, about $\frac{3}{4}$ -inch diameter (as determined visually) pulling was initiated at a rate of 0.100 inches per hour. The crystal was pulled to a length of $\frac{3}{8}$ inch and then "burned in", to reduce the number of grains and defects. The crystal was then allowed to grow out to $\frac{3}{4}$ -inch diameter and growth control was maintained until a 3-inch length of crystal was obtained. The crystal was "burned off", i.e. separated from the remaining melt and slowly cooled to room temperature.

The resulting crystal was strain-free and had excellent color change with wavelength of incident light. The resulting crystal weighed 400 carats. Conventional chemical or spectrographic analysis of the crystal is used to determine the specific amounts of iron and chromium in the crystal.

Example 2

Using the flux melt technique, the following parameters were used: 8500 grams of lithium polymolybdate, 61.07 grams of beryllium oxide, 249.18 grams of aluminum oxide, 0.38 grams of chromium oxide, and 9.18 grams of iron oxide. Mixing these compounds together and heating the same to a temperature of about 1200°C and allowing crystalline growth on a seed of chrysoberyl, a crystal was formed which has color change characteristics substantially the same as those of natural alexandrite. The crystal had iron of about 0.3% by weight of the crystal and chromium of about 0.7% by weight of the crystal.

Alexandrite, a variety of chrysoberyl, is valued as a gemstone because of its unique color change, which is commonly observed as a raspberry red color in tungsten light and a definite green in sunlight.

This color change has previously been erroneously attributed to dichroism. It has also been attributed to Cr^{+++} in octahedral coordination, but systematic work by us has demonstrated that the observed color change in alexandrite could not be brought about by doping with chromium alone. It required a parametric study to determine that Fe was the essential element that had to be added to the Cr to bring about the change of color with the change of wavelength in the incident light. A green color can be attained using vanadium as the dopant, but no color change is observed.

While the foregoing has described the melt as being progressively cooled during the time the seeds are maintained therein, it is possible to keep the temperature substantially constant so that there is a temperature gradient across the melt. In such a case, the nutrient will be in the hotter part of the melt and the seeds will be placed in the cooler part. Growth on the seeds would occur as discussed above. Cooling of the seeds and the growth thereon would be accomplished after the same are removed from the melt.

In the foregoing description the flux material was described as being lithium polymolybdate. Other compounds could be used as the flux material, such as niobate, tungstate and lead-oxyfluoride. The nutrient material could be any one or group of beryllium and aluminum compounds other than beryllium oxide and aluminum oxide as described above. Also, compounds other than the two described above containing iron and chromium could be used. Such other compounds should contain iron in the range of 0.7% to 2.8% by weight of the melt and chromium in the range of 0.0000685% to 0.5130% by weight of the melt. We claim:

1. A synthetic gem-like crystal simulating the color change characteristic of natural alexandrite when illuminated by daylight and by tungsten light, characterized in that the crystal is grown on a chrysoberyl seed in a melt containing a flux material, a nutrient material having beryllium and alumina therein and dopant material containing iron and chromium, with the iron in the melt being in the range of approximately 0.07% to 3.0% by weight of the melt and the chromium in the melt being in the range of approximately 0.0000685% to 0.5130% by weight of the melt, the iron in the crystal being in the range of approximately 0.07% to 4.89% by weight of the crystal and the chromium in the crystal being in the range of approximately 0.0342% to 2.052% by weight of the crystal.

2. A crystal as set forth in claim 1, wherein the melt has a temperature in the range of about 1100°C. to 1300°C. and said flux material provides approximately 95% by weight thereof, said nutrient material providing approximately 4% by weight of the melt, and the dopant material providing approximately 1% by weight of the melt.

3. A crystal as set forth in claim 2, wherein said flux material is lithium polymolybdate, said nutrient material being beryllium oxide and aluminum oxide, said dopant material including a mixture of iron oxide and chromium oxide.

4. A crystal as set forth in claim 3, wherein the iron oxide in the melt is in the range of 0.1% to 4.0% by weight thereof and the chromium oxide in the melt is in the range of 0.0001% to 0.5% by weight thereof.

5. A crystal as set forth in claim 1, wherein the melt has a temperature at least equal to the melting point of chrysoberyl, the crystal being further characterized in that, after deposit of the seed in the melt, the seed is pulled from the melt at a controlled rate as at least part of the seed is maintained in the melt during said period to cause a predetermined amount of the crystal to grow on the seed, removing the crystal and seed from the melt, and allowing the crystal and seed to cool to a preselected temperature.

6. A synthetic gem-like crystal comprising: a body having an orthorhombic crystalline structure and formed by being grown synthetically from a seed of

chrysoberyl in a flux melt containing a flux material providing approximately 95% by weight of the mixture, a nutrient material providing approximately 4% by weight of the mixture, and a dopant material providing approximately 1% by weight of the mixture, with said dopant material containing iron in the range of about 0.7% to 1% by weight of the melt and chromium in the range of about 0.00007% to 0.5130% by weight of the melt, whereby the body, when formed, contains iron and chromium in the ranges of about 0.07% to 4.89% and 0.0342% and 2.052%, respectively, by weight of the melt to assure that the body exhibits changes in color when illuminated by daylight and by tungsten light, with said color changes being sufficient to cause the body to simulate natural alexandrite under substantially the same conditions of illumination.

7. A composition of matter for use in making a synthetic crystal which simulates the color change characteristic of natural alexandrite in daylight and in tungsten light comprising: a mixture including a flux material, a nutrient material beryllium and alumina and a dopant material having iron and chromium therein, with the iron in the mixture being in the range of 0.07% to 3.0% by weight thereof and the chromium in the mixture being in the range of 0.0000685% to 0.5130% by weight thereof; the mixture adapted to be heated to a temperature in a predetermined range to form a melt is saturated so that, upon depositing a seed of chrysoberyl in the melt, growth will appear on the seed to form said crystal and the crystal will contain iron in the range of 0.07% to 4.89% by weight of the crystal and chromium in the range of 0.0342% to 2.052% by weight of the crystal, whereby the iron and chromium will provide the aforesaid color change characteristics for the crystal in daylight and in tungsten light to cause the crystal to substantially simulate natural alexandrite.

8. A composition of matter as set forth in claim 7, wherein said mixture includes flux material providing approximately 95% by weight of the mixture, the nutrient material providing approximately 4% by weight of the mixture, and the dopant material providing approximately 1% by weight of the mixture.

9. A composition of matter as set forth in claim 8, wherein said flux material is selected from the group including lithium polymolybdate, vanadium pentoxide, and lead oxyfluoride.

10. A composition of matter as set forth in claim 7, wherein said nutrient material includes beryllium oxide and aluminum oxide, said dopant material includes iron oxide and chromium oxide.

11. A composition of matter as set forth in claim 10, wherein the iron oxide in the mixture is in the range of 0.1% to 4.0% by weight thereof, and the chromium oxide in the mixture is in the range of 0.0001% to 0.5% by weight thereof.

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UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION

PATENT NO. : 3,912,521

DATED : October 14, 1975

INVENTOR(S) : Carl F. Cline and David A. Patterson

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In the listing of the inventors, add the name "Donald D. Kingman" after the names Carl F. Cline and David A. Patterson

Signed and Sealed this

twentieth Day of January 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks