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J. P. REMEIKA

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GROWTH OF SINGLE CRYSTALS OF CORUNDUM AND GALLIUM OXIDE

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FIG. 1

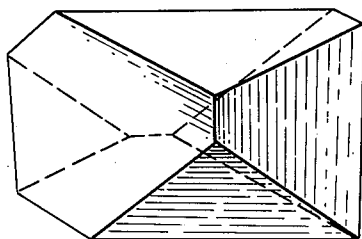
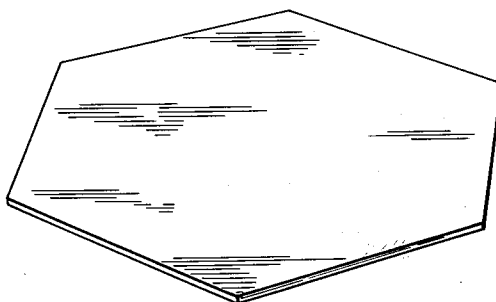


FIG. 2



INVENTOR
J. P. REMEIKA
BY
George S. Erdig
ATTORNEY

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GROWTH OF SINGLE CRYSTALS OF CORUNDUM AND GALLIUM OXIDE

Joseph P. Remeika, Berkeley Heights, N.J., assignor to Bell Telephone Laboratories, Incorporated, New York, N.Y., a corporation of New York

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9 Claims. (Cl. 23—305)

This invention relates to a method for growing single crystals of gallium oxide and materials in the corundum system in a flux comprising lead oxide and boron oxide.

As applied to corundum the present invention represents a method for growing single crystals of such material by spontaneous nucleation. This method permits a flexibility in that in addition to preparing corundum crystals of the customary rhombohedral habit there is also produced corundum crystals of a hexagonal plate structure which, so far as can be ascertained, have not been reported in the literature. The required conditions for the preparation of each of these materials is discussed below.

The gallium oxide crystals produced by the present method are of rectangular bar habit and are of a magnitude which is greater than that heretofore obtained by the prior art methods. This result is attributed to the use of the novel flux of this invention. The general conditions for the growth of these materials are the same as for the growth of corundum as discussed below.

Both the gallium oxide and the corundum materials prepared by the present inventive method are of particular interest for use as the host lattice in maser applications.

The particular habit of crystal growth that obtains is dependent upon the temperature at which initial nucleation occurs. Generally, it may be stated that crystallization initially occurring at temperatures near the maximum of 1300° C. result in a rhombohedral habit, while plate-habit is favored for formation below about 1250° C., with a preferred initial crystallization for plate-like habit in the range of 1225° to 1250° C. for maximum yield. Hexagonal plate-habit growth is observed for initial nucleation as low as of the order of 900° C. Variations in either or both of two conditions result in maximum yield of either crystalline habit. Formations in flux ratios (B_2O_3 to PbO) effecting a decreased solubility have a given amount of nutrient, result in nucleation at a higher temperature, therefore, preference for the rhombohedral habit. The same result may be obtained by increasing the amount of nutrient for a given ratio so producing nucleation at higher temperature. It follows that plate-like growth is favored by conditions causing greater solubility, that is for a nutrient flux solution at a lower percentage of saturation at a given temperature, conditions favoring greater solubility being increased B_2O_3 to PbO ratio and/or decreased nutrient to flux ratio. The only limitation on these general considerations is that the boron content may not be increased above a ratio of about 12 to 50, this resulting in excess borate formation.

The invention will be more readily understood by reference to the following descriptions taken in conjunction with the accompanying drawings forming a part thereof, and from the appended claims. In the drawings: FIG. 1 depicts a corundum crystal of rhombohedral form. FIG. 2 depicts a corundum crystal of a hexagonal plate-habit.

Referring more particularly to the drawings, FIG. 1 shows by way of example and for purposes of illustration a corundum crystal of rhombohedral habit.

In growing crystals of the type shown in FIG. 1 the ideal flux ratio is of the order of 1 to 50 parts of boron oxide to lead oxide. The ideal nutrient to flux ratio for this flux is 6.80 parts of aluminum oxide to 51 parts of

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flux. The upper limit on this quantity is saturation at the maximum temperature of 1300° C. A lower limit must be carefully set since initial nucleation must occur above about 1275° C. to avoid plate-like growth. For the particular flux ratio initial nucleation will occur at 1275° to 1300° C. only over the flux range of from 6.85:51 to 6.70:51. However, the ratio may be increased slightly by increasing the maximum temperature although it is considered practical to operate only up to a temperature of the order of 1300° C., since excessive volatilization of the boron oxide flux ingredient occurs above this temperature. The other alternative is to vary the flux ratio. Further decreasing the amount of boron in the flux permits growth of rhombohedral crystals for lesser nutrient ratios, however, resulting also in decreased yield. The low limit on the flux ratio is about 1 part boron oxide to 100 parts lead oxide at which the gross nutrient ratio is about one-half. Increasing the boron oxide content requires a corresponding increase in nutrient to flux ratio, so that doubling the boron content permits increasing the gross ratio to about 7.0:51 to 7.2:51. A limitation on this variation is imposed by the increased viscosity of the system, resulting in, first super cooling and, subsequently, a large number of nucleation centers and, consequently, a large number of small crystals of the plate-habit. The upper limit on boron oxide to lead oxide at rhombohedral growth occurs at about 2 to 50.

FIG. 2 shows a corundum crystal of a hexagonal plate-habit.

In growing the crystals of the type shown in FIG. 2 the preferred flux composition for producing a maximum yield of crystals of this habit is of the order of 4 parts of boron oxide to 50 parts of lead oxide. When employing this ratio it has been found that 7.3 parts by weight of aluminum oxide is most desirable. Hexagonal plate-habit is predominant for crystals which nucleate in or below the temperature range of 1225° to 1250° C. The conditions favoring nucleation from 50° to 75° below the maximum temperature of 1300° C. are:

(a) Increase in boron oxide to lead oxide ratio, thus increasing the necessary amount of nutrient to saturate the solution at a given temperature and

(b) Decrease in the gross nutrient to flux ratio.

Since there is no other habit below temperatures in the crystallization ranges set forth above, there is no absolute lower limit above the temperature at which the entire nutrient has crystallized (about 850° C.). Total crystallization may be brought about at temperatures as low as 500° C. resulting in a highly viscous plastic-like mass containing a multitude of small crystals. The ideal amount of nutrient for a 54 unit flux is indicated above as 7.3 parts by weight with a preferred range being of the order of 7.2 to 7.4 parts by weight. Variation beyond these limits results in a decrease in plate yield of greater than 30 percent. The effect of further decreasing the amount of nutrient results in less nutrient in solution and, therefore, a decrease in yield while a further increase results in a certain amount of rhombohedral growth before plate-like growth commences.

Employing 7.3 units of nutrient it has been determined that the preferred range of boron oxide to lead oxide is in the range of 3:50 to 5:50. Varying the ratio in the flux beyond these limits results in a decrease in yield of greater than 30 percent.

It is possible to obtain a mixed product including both rhombohedral and hexagonal crystals using intermediate conditions, either nutrient to flux or boron oxide to lead oxide.

In order that those skilled in the art may more fully understand the inventive concept herein presented the following examples are given by way of illustration and not limitation.

EXAMPLE 1

A mixture of 50.0 grams of lead oxide, 1.0 gram boron oxide and 6.80 grams of aluminum oxide was prepared in a platinum crucible and covered with a platinum lid. The crucible was next placed into a horizontal globar furnace with a silicon carbide muffle and a mullite floor plate and the crucible, together with contents was heated to a temperature of 1300° C. and maintained at this level for a period of 8 hours. Controlled cooling at the rate of 2° per hour from the maximum of 1300° C. was then commenced by a controlled energization of the furnace. This program was continued until a temperature of about 915° C. was reached. At this point the crucible was removed from the furnace and the still liquid portion was poured off. After pouring off the liquid the crystals still in the crucible were permitted to cool by reason of their relatively small volume. The crucible was then immersed in a vessel containing a dilute solution of nitric acid and water. This acid cleaning procedure was continued until all flux residue has been removed from the crystals. Subsequent to this acid solution was poured off, the crucible removed from the container, and the crystals washed in three successive rinses of boiling distilled water. Following this treatment, the crystals were dried by air drying at room temperature. The yield was approximately 4.2 grams. Maximum crystal size was of the order of ½ centimeter at its longest dimension. The crystal was colorless and transparent in full size.

EXAMPLE 2

A mixture of 50.0 grams of lead oxide, 4.0 grams of boron oxide and 7.30 grams of aluminum oxide was prepared in a platinum crucible and the procedure of Example 1 repeated. The yield was approximately 4.6 grams. Maximum crystal size was of the order of 3 centimeters. Analysis revealed the material to be aluminum oxide of a hexagonal plate-habit, colorless and transparent.

EXAMPLES 3 THROUGH 5

Example 1 was rerun using the indicated amounts of additives, which as discussed above add coloration to the material and may produce fluorescence and serve as the excitation ion for maser use. Since the amount of additive was slight it was not necessary to vary the overall amounts of other ingredients. Larger amounts of additive than set forth below are feasible but not generally indicated for any of these purposes.

Table

Example	Additive	Percent by Weight	Color
3-----	Cr ₂ O ₃	1.0 (.0975 gram)-----	Light Ruby Red.
4-----	Co ₂ O ₃	2.0 (.2204 gram)-----	Pale Green.
5-----	Fe ₂ O ₃	3.0 (.3240 gram)-----	Pale Yellow.

In the following examples the procedure of Example 2 was repeated with the addition of additives. The resultant crystals were of a hexagonal plate-habit.

Table

Example	Additive	Percent by Weight	Color
6-----	Cr ₂ O ₃	5.0 (.4875 gram)-----	Deep Red.
7-----	Fe ₂ O ₃	0.01 (.0108 gram)-----	Virtually Colorless.
8-----	Cr ₂ O ₃	0.1 (.0104 gram)-----	Virtually Colorless (fluorescent in UV at room temperature).
9-----	Co ₂ O ₃	4.0 (.4800 gram)-----	Medium Green.

EXAMPLE 10

A mixture of 50 grams of lead oxide, 3 grams of boron oxide and 10 grams of gallium oxide was prepared in a platinum crucible and the procedure of Example 1 repeated. The yield was approximately 5.5 grams. Maxi-

mum crystal size was of the order of 0.5 centimeter. Analysis revealed the material to be Ga₂O₃—Colorless—Transparent in full section.

Crystals discussed in the examples were produced by cooling at the rate of two degrees per hour, at least over the crystallization range. In the instance of hexagonal plate-like growth, the cooling rate has been found to be particularly critical, appreciably greater rates resulting in entrapment of fluxes between laminae and, also, in severe cases, in arrest of laminar growth, so resulting in a step configuration. This rate suggests that plate-like growth occurs, at least initially, in a laminate of a finite thickness. These factors become significant at cooling rates of the order of about 7° C. per hour. It appears that the thickness of the initial laminate to nucleate is a function of the rate of crystallization at that temperature, so that the effect of supercooling, so resulting in increased rate of crystal growth when nucleation finally does occur, is to decrease the thickness of any laminae nucleated at that temperature.

It should be noted that, although the predominant growth direction is such as to produce the hexagonal plate-habit, growth does occur in a normal direction at a proportional rate which may be determined from the ratio of thicknesses of the final crystal. Accordingly, it may be stated that the number of laminae for a given plate thickness may be decreased for decreasing rate of crystallization with a limiting condition existing that large plates of but a single laminate may be produced for extremely slow rates of crystallization, e.g., substantially below about 1° C. per hour.

Although it is not necessary, acid separation may be minimized by pouring off the liquid content of the melt at a temperature corresponding with or above total nutrient crystallization. This temperature varies from about 850° C. to about 950° C. for the preferred ratios discussed. This alternative procedure is well known to those skilled in the art.

It is to be appreciated that the examples set forth above are intended merely as illustrative and not by way of limitation. 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 growing single crystals comprising at least one member selected from the group consisting of aluminum oxide and gallium oxide which comprises heating said material together with a mixture of lead oxide and boron oxide the weight ratio of boron oxide to lead oxide being within the approximate range of 1:100 to 10:100 and cooling the resultant melt.

2. The method of growing single crystals of aluminum oxide of a rhombohedral habit which comprises heating a nutrient consisting essentially of aluminum oxide in a flux comprising a mixture of boron oxide and lead oxide, the weight ratio of boron oxide to lead oxide being in the approximate range of 1:25 to 1:100, the weight ratio of nutrient to flux being within the approximate range of 6.85:51 to 6.70:51, and cooling the resultant melt.

3. The method according to the procedure of claim 2 wherein the weight ratio of boron oxide to lead oxide is approximately 1:50.

4. The method of growing a single crystal of aluminum oxide of a hexagonal plate habit which comprises heating a nutrient consisting essentially of aluminum oxide in a flux comprising a mixture of boron oxide and lead oxide, the weight ratio of boron oxide to lead oxide being in the approximate range of 3:50 to 5:50, the weight ratio of nutrient to flux being within the approximate range of 7.2:54 to 7.4:54, and cooling the resultant melt.

5. The method according to the procedure of claim 4 wherein the weight ratio of boron oxide to lead oxide is 4:50.

6. The method according to the procedure of claim

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4 wherein the weight ratio of nutrient to flux is approximately 7.3:54.

7. The method of growing single crystals of rhombohedral habit of aluminum oxide containing chromium which comprises heating a nutrient consisting essentially of aluminum oxide and chromium oxide in a flux comprising boron oxide and lead oxide, the weight ratio of boron oxide to lead oxide being in the approximate range of 1:25 to 1:100, the weight ratio of nutrient to flux being within the approximate range of 6.85:51 to 6.70:51, and cooling the resultant melt.

8. The method of growing single crystals of hexagonal plate habit of aluminum oxide containing iron which comprises heating a nutrient consisting essentially of aluminum oxide and iron oxide in a flux comprising a mixture of boron oxide and lead oxide, the weight ratio of boron oxide to lead oxide being in the approximate range of 3:50 to 5:50, the weight ratio of nutrient to flux being within the approximate range of 7.2:54 to 7.4:54, and cooling the resultant melt.

9. The method of growing single crystals of gallium oxide which comprises heating a nutrient consisting

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essentially of gallium oxide in a flux comprising boron oxide and lead oxide, the weight ratio of boron oxide to lead oxide being in the approximate range of 1:25 to 1:100.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,075,831

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Joseph P. Remeika

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 5, for "globar" read -- Globar --.

Signed and sealed this 12th day of November 1963.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

EDWIN L. REYNOLDS

Acting Commissioner of Patents