

1

2

3,595,803 METHOD FOR GROWING OXIDE SINGLE CRYSTALS

Cortland O. Dugger, 118 Fayerweather St.,
Cambridge, Mass. 02138

No Drawing. Continuation-in-part of application Ser. No. 619,132, Feb. 24, 1967. This application Sept. 4, 1969, Ser. No. 855,426

Int. Cl. C09k 1/68

U.S. Cl. 252—301.4

9 Claims

ABSTRACT OF THE DISCLOSURE

A method for forming stoichiometrically proportioned refractory oxide single crystals from a mixture of a cationic halide such as magnesium fluoride and a cationic oxide such as aluminum oxide, in which the cations from both the halide and the oxide form the multiple cationic components of the resultant crystalline material. The method involves the steps of heating the mixture to a temperature slightly above its melting point for about one hour to effect an apparent hydrolysis of the halide and form a homogenous melt followed by the step of cooling the melt within a programmed cooling rate range of from about 0.5° C. per hour to about 10° C. per hour to a temperature which is slightly above the solidification point of the melt.

BACKGROUND OF THE INVENTION

This is a continuation-in-part of application Ser. No. 619,132 filed Feb. 24, 1967, now abandoned.

This invention relates to a method of growing high quality oxide single crystals and to the single crystals formed thereby. More particularly, this invention relates to a method for growing stoichiometrically proportioned crystalline materials from a molten solution of a hydrated halide or from a molten solution comprising a mixture of a hydrated halide and an oxide. The cations from both the halide and the oxide form the cationic components of the resultant crystalline material.

Heretofore, the growth of stoichiometric spinel single crystals has proven to be extremely difficult. The crystals so grown have not been well formed and lack the degree of perfection needed for use in applications such as laser beams, filters, isolators, power limiters and harmonic generators. With the present invention, however, it has been found that oxide single crystals can be formed through an apparent thermal hydrolysis of a hydrated halide whose cation is the same as the cation of the desired oxide single crystal. The resultant crystals are mechanically sound, relatively free of foreign inclusions, have well developed crystalline faces and possess a high degree of overall quality that permits their use in critical microwave and coherent radiation applications.

SUMMARY OF THE INVENTION

In accordance with this invention, it has been found that crystal growth can be attained by what appears to be the partial or complete thermal hydrolysis of a hydrated halide. In general, the method involves the steps of forming a starting mixture which comprises about 15 to 90 mole percent of a hydrated halide, or mixture of halides, whose cations form at least one of the desired crystal constituents with the balance of the mixture being an oxide, or mixture of oxides, whose cations form the other crystal constituents. The mixture is heated in an appropriate crucible in a non-oxidizing atmosphere to a temperature of from about 80° C. to 1800° C., or slightly above the melting point of the mixture, in order to form a molten solution. The molten solution is maintained at

the elevated temperature for a sufficient period of time, generally about one hour, to insure complete dissolving of all of the components of the mixture. Preferably, the temperature of the molten solution is then slowly cooled at a programmed cooling rate of from about 0.5° C. to about 10° C. per hour until the temperature of the solution reaches a point slightly above the solidification point temperature of the solution. This is followed by rapid cooling at a rate of from about 200° C. to about 500° C. per hour to room temperature. However, crystallization can be induced by any of the well known crystal growing techniques, such as Czochralski, Bridgman and others of like character. The apparent hydrolysis of the hydrated halide can also be effected by heating the halide component by itself without the addition of the oxide component.

The invention provides a method for growing high quality stoichiometric spinel single crystals, such as magnesium aluminate. Heretofore, stoichiometric magnesium aluminate was not known to be available. The invention also provides a method for growing other multiple oxide single crystals of the spinel group, the garnet group, orthosilicates and zirconates. For example, crystals such as yttrium iron garnet, yttrium aluminum garnet, barium zirconate, lanthanum aluminate, barium sodium niobate, potassium tantalum niobate, magnesium oxide, zinc oxide, a double salt of magnesium orthosilicate and magnesium fluoride (forsterite) have been grown and verified by X-ray analysis in accordance with the method of this invention.

Accordingly, the primary object of this invention is to provide a novel and simplified method for forming high quality refractory oxide single crystals.

Another object of this invention is to provide a method for growing transparent oxide single crystals of the spinel group.

A further object of this invention is to provide a method for growing spinel crystals through what appears to be the hydrolysis of a hydrated halide whose cation forms at least one constituent of the desired spinel crystal.

Still a further object of this invention is to provide a simplified technique for growing transparent multiple oxide single crystals that are substantially free from defects, have well developed crystalline faces and are mechanically sound to the point that makes them valuable for use in microwave and coherent radiation devices.

Still further objects, advantages and features of this invention will become apparent upon consideration of the following detailed description thereof.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the method of this invention, the apparent partial or complete thermal hydrolysis of the hydrated halide salt is effected by the conversion of some or all of the hydrated halide to an oxide at temperatures of from about 80° C. to 1800° C. This conversion seems to occur because the water chemically bound to the halide as a hydrate reacts with the halide as the temperature is raised; hydrogen halide is given off as a gas, leaving the oxygen anion (negative charge) of the water molecule very reactive ("activated"). The "activated" oxygen anion reacts with a cation (positive charge) to give the respective cationic oxide.

The growth of a crystal from the molten halide solution is effected by the precipitation or crystallization of the solute (the desired crystalline end product) from the molten solution. The solution consists of the solute components and the molten solvent components. The molten solvent components are considered to dissolve the solute components under the specified reaction conditions encompassed within the scope of the invention.

3

The precipitation or crystallization of the crystal from the solution is in turn brought about by employing various crystal growing methods. One of these methods includes the technique of slow cooling over a constant period of time at a predetermined rate. The temperature of the molten solution is cooled at a programmed rate to a point slightly above the freezing point or solidification point of the solvent. The programmed cooling rate maintains a slight supersaturation of the solute in the molten solution. The slight supersaturation of the solute in the molten solution is the driving force which enhances crystallization.

Another method for effecting crystallization is the Czochralski method which consists of lowering a rod of the material of which the crystal is to be formed into a crucible containing a molten solvent for the crystal forming material. The rod of crystal forming material is then very slowly retracted upward at a carefully controlled rate of speed, with the result that a single crystal of material is grown on the end of the rod. The Bridgman method, another crystal growing technique, involves lowering a cone shaped crucible containing molten material to be crystallized through a region in which a temperature gradient is maintained such that the upper portion of the region is above the melting point of the material, while the lower portion of the region is below that melting point. Any of the above methods of cooling the crystal forming material to effect crystallization may be employed with the present invention. However, it has been found that optimum results are obtained by using the slow cooling or programmed cooling technique referred to above.

In the case of a partial thermal hydrolysis of a hydrated halide-oxide mixture, it is preferable that the following conditions prevail: (a) the concentration ratio of the hydrated halide to the hydrated oxide be large. This is to insure that following the partial thermal hydrolysis of some of the halide, there will be enough remaining halide in the molten state to serve as a solvent for the oxide. The amount of hydrolysis can depend upon the state of the oxide, that is, if the oxide is hydrated, since either a hydrated or anhydrous oxide salt can be employed as the oxide component of the mixture, (b) the halide in molten solution should be thermodynamically stable in the presence of oxygen ions; and (c) at least one of the cationic halides chosen as a solvent must be one of the desired crystal components.

In the case of complete thermal hydrolysis of a hydrated halide-oxide mixture, it is preferable that an inert cationic halide or cationic oxide serve as the solvent for the desired crystal component oxide. For example, magnesium chloride ($MgCl_2$) completely hydrolyzes rapidly at elevated temperatures in the presence of water to magnesium oxide (MgO). If hydrated magnesium chloride is intimately mixed with hydrated aluminum oxide and the temperature is raised, magnesium chloride will completely hydrolyze to magnesium oxide below the melting point of magnesium chloride (M.P. $708^\circ C.$). As the temperature is continually raised, a solid state reaction between magnesium oxide and aluminum oxide occurs forming magnesium aluminate ($MgAl_2O_4$). A liquid (melt) state for $MgAl_2O_4$ does not occur until approximately $2135^\circ C.$ which is out of the temperature range ($80^\circ C.$ to $1800^\circ C.$) of this invention. However, if an inert halide is added at room temperature to the intimately mixed hydrated magnesium chloride and hydrated aluminum oxide, to serve as a solvent for the converted magnesium chloride to magnesium oxide and the aluminum oxide, then the resulting magnesium aluminate phase may be crystallized from solution below the maximum ($1800^\circ C.$) temperature of this invention.

An inert halide is understood to mean a material whose cations are not included in the desired crystal as a major constituent. Barium fluoride, when used in proportions of from about 20 to 80 mole percent of the halide material having an ion common to the ion in the molten solu-

4

tion, has been found to be an excellent inert material. The purpose of using an inert halide is to lower the vapor pressure of the common ion halide. The common ion halide is incorporated in the crystal as well as in the molten solution. The inert halide is not found in a large concentration in the desired crystal since it is not included as an intentional ingredient.

The high quality and large crystal size, which is the most striking characteristic of the hydrolysis-molten solution technique of this invention, appears to be due to the formation of very reactive oxygen anions by the halide hydrolysis. These anions, which are uniformly distributed throughout the solution, enhance the rate of crystallization of the desired oxide by chemically combining with the cations in solution.

The following information is presented as experimental evidence in support of the hypothesis that a partial thermal hydrolysis of a hydrated halide, such as magnesium fluoride (MgF_2), takes place in the method of this invention. A second halide, such as barium fluoride (BaF_2), is used as the "inert" halide solvent for the oxide constituent of the desired crystal.

Samples of a pure hydrated equimolar mixture of $BaF_2 \cdot MgF_2$ were heated in an open vessel under a dried helium atmosphere and both the change in weight of the sample and the fluoride content in the exit gas was measured. Some fluoride appeared in the exit stream at temperatures as low as $73^\circ C.$ The formation of volatile fluorides continued up to sample temperatures of $1250^\circ C.$ The BaF_2 and MgF_2 are not appreciably volatile at these temperatures and the fluoride observed in the exit gas was hydrogen fluoride.

Differential thermal analysis (DTA) indicated a wide temperature range in which the hydrolysis of $MgF_2 \cdot xH_2O$ occurred. Reaction peaks were observable at $73^\circ C.$, $139^\circ C.$, $400^\circ C.$, $501^\circ C.$, $692^\circ C.$, $902^\circ C.$, $920^\circ C.$, $1030^\circ C.$, $1128^\circ C.$ and $1250^\circ C.$ The presence of MgO in the DTA samples was confirmed by Debye Scherrer X-ray patterns. While the indicated hydrolysis temperatures are below the melting point of MgF ($1263^\circ C.$), the higher hydrolysis temperatures are above the melting point of the equimolar $BaF_2 \cdot MgF_2$ molten solution (M.P. $977^\circ C.$). Differential thermal analysis of the equimolar $BaF_2 \cdot MgF_2$ show the same patterns of reaction as for pure hydrated MgF_2 . A portion of the hydrolysis occurs in the molten phase.

To insure that the source of MgO was not due to oxygen in the atmosphere or ambient water vapor, the carbon heated furnace in which all of the crystal growth experiments were performed had been previously outgassed under 10^{-3} mm. of Hg vacuum at $2500^\circ C.$ for eight hours. At the beginning of each crystal growth experiment all moist air was removed by purging the furnace four times each at room temperature and at $300^\circ C.$, using both a vacuum and helium gas passed through a Linde molecular sieve immersed in liquid nitrogen and a Mickel purifying gas unit. From a theoretical consideration it would appear that the MgO was formed by the chemical reaction of magnesium fluoride with its water of hydration and, possibly, by the chemical reaction of magnesium fluoride and the aluminum oxide waters of crystallization. In the presence of Al_2O_3 , the alkaline earth fluoride solvents also partially hydrolyze due to the chemically bound water supplied from several hydrates of Al_2O_3 (diaspore), ($Al_2O_3 \cdot H_2O$), bauxite ($Al_2O_3 \cdot 2H_2O$), and gibbsite ($Al_2O_3 \cdot 3H_2O$).

The high crystal quality and large size, which is the most striking characteristics of the hydrolysis molten-solution technique of this invention, appears to be due to: (a) The formation of "activated" oxygen anions by the halide hydrolysis mechanism. These anions are uniformly distributed throughout the solution. The "activated" anions which combine with magnesium cations (Mg^{+2}) and aluminum cations (Al^{+3}) in an equimolar molten barium fluoride (BaF_2) and magnesium fluoride (MgF_2)

solution appear to be more chemically reactive than oxygen ions added as magnesium oxide either stoichiometrically or excessively to a molten salt solution of BaF_2 (neutral salt) and aluminum oxide (Al_2O_3), (b) the magnesium ion (Mg^{+2}) which was common to both the solvent and the growing spinel crystals (solute), the common magnesium ion reduced the solubility of spinel in solution and made the transition from the molten phase to the solid phase as gradual as possible, (c) the addition of BaF_2 as a second solvent.

Spinel single crystals grown from a molten solution of MgF_2 and Al_2O_3 only, were of high quality, well formed octahedrally shaped crystals but extremely small. Adding an equimolar concentration of BaF_2 to MgF_2 resulted in the growth of larger crystals because of a reduction in the large excess of common ion; and a reduction of the spinel supersaturation by diluting the solution. The gradual transition of spinel from the molten phase to the solid phase is due to the common ion and the addition of BaF_2 reduced the number of spontaneous crystal nucleations and permitted a larger crystal to grow by the redissolving of smaller crystals.

With the foregoing general discussion in mind there are presented herewith detailed specific examples which illustrate to those skilled in the art the manner in which this invention is carried out in effect. Example 1 discloses a process for growing a spinel such as stoichiometric magnesium aluminate single crystals; Example 2 presents a method for growing barium magnesium aluminate; Example 3 presents a method for growing yttrium iron garnet; while Examples 4 to 7 illustrate still other embodiments of the invention.

Example 1

Transparent magnesium aluminate (1 mole MgO /1 mole Al_2O_3) single crystals, doped with chromium sesquioxide (Cr_2O_3), were grown from a molten salt solution following the hydrolysis of some of the MgF_2 to MgO and the chemical formation and dissolution of the magnesium aluminate phase. The starting composition of the mixture was 38.1 mole percent BaF_2 , 38.1 mole percent $\text{MgF}_2 \cdot x\text{H}_2\text{O}$ weighed as MgF_2 , 23.8 mole percent Al_2O_3 , and 200 p.p.m. Cr_2O_3 . The largest octahedral crystals measured 4 mm. from apex to apex and 3 mm. across. Polarizing microscopy, Laue, and Debye-Scherrer X-ray analyses confirm the isotropic character, monocrystallinity, and spinel structure of the crystals, respectively.

The thermal hydrolytic reactions of some of the MgF_2 to MgO , the chemical formation of spinel (MgAl_2O_4), and the dissolving of the spinel in the molten salts, plotted by differential thermal analysis, occurred within the temperature range of 155° C. to approximately 1642° C. Upon programmed cooling at 1642° C., recrystallization of the spinel phase was initiated.

The crystals were grown in an open molybdenum crucible, which contained the noncalcined and unreacted starting chemicals. The crucible was heated under a vacuum to 900° C. in a carbon furnace. At 900° C., a helium atmosphere was introduced and the temperature raised to 1650° C. This temperature was maintained for three hours and then lowered at approximately 5° C./hour to 1510° C. The furnace was then rapidly cooled (500° C./hour) to room temperature. The crystals were removed by destroying the crucible and gently tapping the matrix with a hammer. The crystals easily separated from the crystallized fluoride solvent. The X-ray density, lattice parameter, and the refractive index of the crystals were 3.577 g./cm.³, 8.0835 Å, and 1.710, respectively. Navias reported for $1\text{MgO}/1\text{Al}_2\text{O}_3$, a specific gravity and lattice parameter of 3.578 g./cm.³ and 8.0832 Å, respectively. Wickersheim and Lefever published an index of refraction of 1.708 for the stoichiometric spinel.

It should be noted that a platinum crucible can be used in place of molybdenum and the crucible does not have to be heated up to 900° C. under a vacuum. Any atmos-

phere may be used depending upon the type of furnace. BaF_2 is not needed to grow the spinel single crystals; however, using BaF_2 enhances the growth of larger stoichiometric spinel crystals than those grown by using only $\text{MgF}_2 \cdot x\text{H}_2\text{O}$ in amounts, for example, of 76.2 mole percent.

Example 2

Transparent barium magnesium aluminate single crystals, doped with chromium sesquioxide (Cr_2O_3) were grown from a molten salt solution following the hydrolysis of some of the MgF_2 to MgO and BaO to BaF_2 and the chemical formation and dissolution of the barium magnesium aluminate phase. The starting composition of the mixture was 38.1 mole percent BaF_2 , 38.1 mole percent $\text{MgF}_2 \cdot x\text{H}_2\text{O}$ weighed as MgF_2 , 23.8 mole percent Al_2O_3 , and 200 p.p.m. Cr_2O_3 .

The starting composition was placed in a platinum crucible, covered, heated in air to 1470° C., and then slowly cooled at approximately 1° C./hour to 1200° C. A new compound is formed in which barium is included in the lattice. Single crystals of this new compound demonstrate a hexagonal habit and the largest crystal measures 5 x 5 x 3 mm.

These crystals are uniaxial optically positive crystals whose indices of refraction are 1.700 and 1.716 for the ordinary ray and the extraordinary ray, respectively. X-ray analysis has identified the compound as hexagonal with a c axis equal to 21.56 Å. and an a axis equal to 5.63 Å. Neglecting the chromium ion content, its formula from wet chemical analysis is $\text{BaMgAl}_{10}\text{O}_{17}$, which is isostructural with $\text{NaAl}_{11}\text{O}_{17}$, whose unit cell dimensions are: c equal to 22.48 Å. and a equal to 5.58 Å.

Fluorescence spectra were obtained for the chromium oxide doped barium magnesium aluminate



crystals at liquid nitrogen temperature (77° K.) and room temperature (300° K.). The fluorescence wavelength, which is the same at both temperatures, is 6950 Å. for



Absorption spectra demonstrate that $(\text{BaMgAl}_{10}\text{O}_{17})\text{Cr}$ has two absorption bands, one at 3900 Å. and the other at 5600 Å. Liquid nitrogen and room temperature measurements were made at 5600 Å. The absorption lines are broad and do not change appreciably with temperature.

Example 3

Transparent yttrium iron garnet crystals ($\text{Y}_3\text{Fe}_5\text{O}_{12}$) were grown from a molten salt solution following the hydrolysis of hydrated yttrium fluoride. The starting composition of the mixture was 80 mole percent hydrated yttrium fluoride and 20 mole percent of ferric oxide. The crystals were grown in a molybdenum crucible which was heated to a soak temperature (maximum temperature) of 1250° C. and maintained at this temperature one hour. The crucible was then slowly cooled to 900° C. at a programmed rate of 1° C. per hour, followed by rapid cooling to room temperature. The crystals were removed from the crucible by gently tapping it with a hammer.

Example 4

A molybdenum crucible containing hydrated magnesium fluoride was heated in a non-oxidizing atmosphere to a temperature of 1300° C. in a carbon furnace and maintained at that temperature for about one hour. The temperature was then lowered at a programmed rate of about 1° C./hour to 900° C., followed by cooling to room temperature. The resultant crystals of magnesium oxide were removed from the crucible by gently tapping with a hammer.

Example 5

Yttrium aluminate crystals ($\text{Y}_3\text{Al}_5\text{O}_{12}$) were grown from a molten solution comprising a starting mixture of

50 mole percent hydrated yttrium fluoride and 50 mole percent of aluminum oxide. The crystals were grown in a molybdenum crucible which was heated to a soak temperature of 1660° C. and maintained at that temperature for about an hour. The crucible was the slowly cooled at a rate of approximately 4° C./hour to 1400° C. followed by rapid cooling to room temperature.

Example 6

In this example the same processing conditions of Example 1—except the soak temperature, was 1450° C. and the molten solution was cooled to 1275° C., at a rate of about 5° C. per hour—were utilized to produce magnesium aluminate crystals. Also, the starting mixture comprised about 90 mole percent hydrated magnesium fluoride and 10 mole percent aluminum oxide.

Example 7

A molybdenum crucible containing a starting mixture of 75 mole percent of yttrium fluoride and 25 mole percent of aluminum oxide was heated in a non-oxidizing atmosphere to a temperature of about 1500° C. for one hour. The crucible was then slowly cooled to 900° C. at a programmed rate of about 2° C./hour followed by rapid cooling to room temperature. The resulting yttrium aluminate ($Y_3Al_5O_{12}$) crystals were removed from the crucible by gentle tapping.

Example 8

A molybdenum crucible containing hydrated zinc fluoride was heated in a non-oxidizing atmosphere to a temperature of 950° C. in a carbon furnace and maintained at that temperature for about one-half hour. The temperature was then lowered at a programmed rate of about 4° C./hour to 700° C., followed by cooling to room temperature. The resultant crystals of zinc oxide were removed from the crucible by gently tapping with a hammer.

The method of the invention is generally performed in a non-oxidizing atmosphere; that is, it is performed under either a vacuum, an inert, or a reducing atmosphere, or any combination thereof. If the starting mixture constituents are contained in a closed (sealed) vessel, the atmosphere inside of the closed vessel, while considered oxidizing, can be effective in producing the desired single oxide crystals because the atmosphere inside the sealed vessel is not in equilibrium with the atmosphere outside of the sealed vessel.

Although the starting compositions referred to in Examples 1 and 2 above for the magnesium aluminate (spinel) and the barium magnesium aluminate are the same concentrations, the different end products which result appear to be a function only of the heating cycle and the maximum attained temperature.

The use of chromium sesquioxide as a dopant material is not essential to the growth of the desired single crystals. It is utilized, however, since it produces a desirable pink fluorescence in the final end product.

From a consideration of the foregoing, it can be seen that this invention provides a simple and efficient method for growing high quality single crystals, especially stoichiometrically proportioned crystals. These crystals have proven to be especially valuable for use in laser beam applications.

The process of the invention is applicable to any halide/oxide system provided the halide salt is thermodynamically stable in the oxide. If it is not stable, then a stable halide can be added as an inert material to prevent the unstable halide from completely oxidizing or vaporizing.

I claim:

1. A method of growing oxide single crystals comprising the steps of forming a mixture which comprises about 40 mole percent magnesium fluoride, about 40

mole percent barium fluoride and about 20 mole percent aluminum oxide, heating the mixture in a non-oxidizing atmosphere to a temperature of about 1650° C. for a period of about three hours followed by cooling the heated mixture to a temperature of 1510° C. at a programmed cooling rate of about 5° C. per hour, continuing to cool the heated mixture to its freezing point to form a fused salt, and then further cooling the said fused salt to room temperature whereby single crystals are formed.

2. A method in accordance with claim 1 including the addition to the said mixture of about 200 p.p.m. of chromium sesquioxide.

3. A method of growing oxide single crystals comprising the steps of forming a mixture which comprises about 40 mole percent magnesium fluoride, about 40 mole percent barium fluoride and about 20 mole percent aluminum oxide, heating the mixture in a non-oxidizing atmosphere to a temperature of about 1470° C. followed by cooling the heated mixture to a temperature of about 1200° C. at a programmed cooling rate of 1° C. per hour, continuing to cool the heated mixture to its freezing point to form a fused salt, and then further cooling the said fused salt to room temperature whereby single crystals are formed.

4. A method in accordance with claim 3 including the addition to the said mixture of about 200 p.p.m. of chromium sesquioxide.

5. A method of growing oxide single crystals comprising the steps of forming a mixture which comprises about 80 mole percent yttrium fluoride and about 20 mole percent ferric oxide, heating the mixture in a non-oxidizing atmosphere to a temperature of 1250° C. for a period of about one hour followed by cooling the said mixture to a temperature of about 900° C. at a programmed cooling rate of about 1° C. per hour, continuing to cool the heated mixture to its freezing point to form a fused salt, and then further cooling the said fused salt to room temperature whereby single crystals are formed.

6. A method of growing oxide single crystals comprising the steps of forming a mixture which comprises about 15 mole percent of yttrium fluoride and about 85 mole percent of an equimolar mixture of yttrium oxide and aluminum oxide, heating the mixture in a non-oxidizing atmosphere to a temperature of about 1800° C. for about one hour, cooling the heated mixture to a temperature of about 1200° C. at a programmed cooling rate of 1° C. per hour, continuing to cool the heated mixture to its freezing point to form a fused salt, and then further cooling the said fused salt to room temperature whereby single crystals are formed.

7. A method of growing oxide single crystals comprising the steps of forming a mixture which comprises about 90 mole percent of magnesium fluoride and about 10 mole percent of aluminum oxide, heating the mixture in a non-oxidizing atmosphere to a temperature of about 1450° C. for a period of about three hours followed by cooling the heated mixture to a temperature of about 1275° C. at a programmed cooling rate of about 5° C. per hour, continuing to cool the heated mixture to its freezing point to form a fused salt, and then further cooling the said fused salt to room temperature whereby single crystals are formed.

8. A method of growing oxide single crystals comprising the steps of forming a mixture which comprises about 50 mole percent of hydrated yttrium fluoride and about 50 mole percent of aluminum oxide, heating the mixture in a non-oxidizing atmosphere to a temperature of about 1660° C. for a period of about one hour followed by cooling the heated mixture to a temperature of about 1400° C. at a programmed cooling rate of about 4° C. per hour, continuing to cool the heated mixture to its freezing point to form a fused salt, and then further cooling the said fused salt to room temperature whereby single crystals are formed.

9. A monocrystalline material possessing a hexagonal crystallographic structure and having the chemical formula $\text{BaMgAl}_{10}\text{O}_{17}$.

References Cited

UNITED STATES PATENTS

3,113,109	12/1963	Brixner	252—62.63
3,115,469	12/1963	Hamilton	252—62.63
3,370,963	2/1968	Bonner	106—42

OTHER REFERENCES

Crystal Growth & Crystallography, Report No. TDR-930 (2240-01) TN-2-A Literature Survey, p. 54 (138).

5 ROBERT D. EDMONDS, Primary Examiner

U.S. Cl. X.R.

23—51, 52, 305; 252—62.57