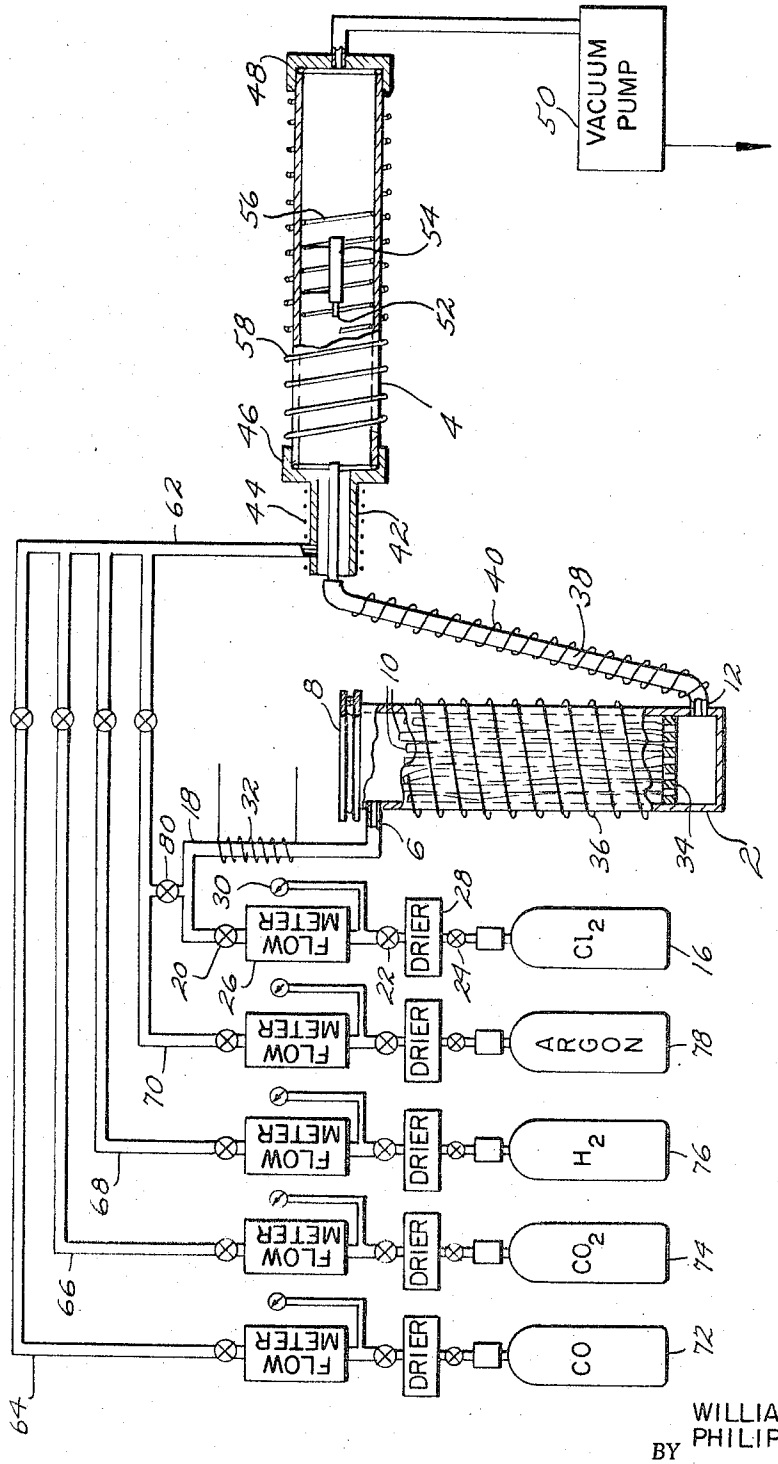
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METHOD OF EPITAXIALLY GROWING METAL OXIDE SINGLE CRYSTALS

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METHOD OF EPITAXIALLY GROWING METAL OXIDE SINGLE CRYSTALS

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ABSTRACT OF THE DISCLOSURE

A method of growing a metal oxide in single crystal form. Metal halide gas is passed through a reaction chamber containing a single crystal substrate at predetermined values of temperature and pressure in the presence of other gases which serve as reaction agents and catalysts, whereupon a solid metal oxide overgrowth in single crystal form is created on the substrate, producing a bulk form single crystal.

This invention relates to the synthesis of single crystals and more particularly to an improved process for growing solid oxide crystals.

A variety of crystal growing techniques have been developed in recent years to meet the needs of different industrial and military applications for relatively large single crystals. These different techniques include the hydrothermal, flux, melt fusion, zone melting, and vapor deposition processes, as well as refinements of the Verneuil flame fusion process. The Verneuil process and the recent refinements thereof, including substitution of a plasma arc in place of a gas flame, have been particularly important in the growth of solid oxide crystals, especially the synthesis of sapphire and ruby crystals. Chemically and physically similar to the natural mineral, synthetic sapphire is grown as a single crystal of high-purity alumina and crystallizes in the hexagonal-rhombohedral crystal system. Ruby (red corundum) differs from white sapphire (clear corundum) in that it has chromium introduced into its crystal lattice during growth. A ruby crystal is essentially the same as a sapphire crystal except for the fact that the color differs and the chromium content introduces a lattice strain.

Although synthetic gem boules can be made successfully by the Verneuil process and the recent refinements thereof, the resultant boules nevertheless suffer from certain limitations, including the presence of impurities in significant quantities, the existence of internal strains whose presence is suggested by relatively high dislocation population, and the requirement for subsequent annealing to prevent boule splitting or fracture. These internal strains are believed due to thermal stresses caused by a temperature gradient at the locus of the growth of the crystal. Additionally the output of a typical Verneuil process suffers from an unusually high incidence of visual imperfections such as non-homogeneous dopant distribution, fused layers caused by incompletely melted powder or to lineage due to variations in internal orientation as seen by differing light refraction through the crystal. Occasionally where the strain is unusually severe, twinning and fracture results. A further disadvantage of the Verneuil process is the use of powdered aluminum oxide as the starting material since the oxide powder must be fused preparatory to crystallizing out on a selected seed crystal. This fusion step requires operation at temperatures in the vicinity of 2000° C. Modifications of the Verneuil system using as the starting material a volatile compound which is converted to the desired oxide by oxidation or hydrolysis, have not been found to be wholly satisfactory because of the difficulty of controlling the reaction and

the problems attendant to condensation of the volatile compound on the walls of the process apparatus.

Accordingly the primary object of the present invention is to provide a new and improved method and apparatus for producing large oxide single crystals which are free of the limitations of the prior art techniques noted above.

A more specific object of the present invention is to provide a method for producing large oxide single crystals of controlled composition having high chemical purity, low internal strain, high crystalline perfection, controlled growth rate, and predetermined crystallographic orientation with respect to growth axis.

A further specific object of the present invention is to provide a process for epitaxially growing single oxide crystals by vapor deposition involving the interaction of depositing vapors with a heated substrate or seed crystal at the solid-vapor interface under controlled conditions of pressure, temperature and supersaturation, the resulting crystals being built up essentially atom by atom, relatively strain free, with high purity and high crystalline perfection. The growth morphology is controlled by orientation of the seed crystal and the growth habit is controlled by pressure and temperature, while the growth velocity is controlled by seed orientation, degree of supersaturation, and temperature.

Other objects and many of the attendant advantages of the present invention will become more readily apparent as reference is had to the following detailed specification when considered together with the accompanying drawing which illustrates a preferred form of apparatus embodying the present invention.

Our process for growing synthetic single crystal bodies will be described in detail hereinafter, for illustration only, as applied to the production of sapphire, ruby and silica crystals. However, it is to be understood that the principles of the process and the apparatus are applicable to the production of crystals having other forms or compositions.

Referring now to the drawing the illustrated apparatus designed and constructed in accordance with the present invention essentially comprises a halide generator **2** and a reaction chamber **4**. The halide generator is a vertical cylindrical unit formed of a non-reactive material such as a stainless steel alloy and comprises an inlet **6** for introduction of a halogen gas, a sealed cover **8** which can be removed for inserting a supply of a selected high purity metal **10** into the unit where it can be reacted with the halogen gas to form a metal halide vapor, and an outlet **12** for passing the metal halide vapor formed in the halide generator to the reaction chamber **4**. In the case of growing sapphire and ruby crystals, according to a preferred embodiment of the invention, the inlet **6** is connected to a pressurized chlorine supply tank **16** via a line **18** which includes appropriate control valves **20**, **22**, and **24**, a flow meter **26**, a drier **28** for removing moisture from the chlorine gas, and a pressure gauge **30**. An electric resistance wire heating element **32** surrounds line **18** and serves to preheat the chlorine gas supplied to the halide generator. This heater is energized from a separately controllable power source (not shown) of conventional design. In the case of sapphire crystals, the high purity metal **10** which is to be converted into a metal halide comprises a group of aluminum strips which are supported within the generator unit on a perforated plate **34** disposed just above the outlet **12**.

Surrounding the halide generator is a second electrical resistance wire heating element **36** which is controllably energized by another suitable power supply (not shown). The heater **36** serves to heat the reactants within the halide generator to the temperature necessary to achieve

generation of a metal chloride according to the following reaction:

$$aM\,(s)+bCl_2\,(g)\rightleftharpoons aMCl_x\,(g)$$

where M is an appropriate metal and *a*, *b* and *x* are whole numbers. For aluminum the reaction is as follows:

$$Al\,(s)+3/2\,Cl_2\,(g)\rightleftharpoons AlCl_3\,(g)$$

The metal halide gas newly formed in the halide generator is delivered to the reaction chamber **4** by means of line **38** which is surrounded and heated by a third electrical resistance heating element **40** which is controllably energized by another separately controllable power supply (not shown). The pipeline **38** is connected to the center tube of a dual concentric tube injector assembly **42** mounted in one end of the reaction chamber **4**. The injector assembly is formed of stainless steel and is surrounded by a fourth electric resistance heater coil **44** which is energized by another separately controllable power source (not shown). The reaction chamber **4** is essentially a horizontally extending vacuum furnace formed of alumina tubing and fitted with removable nonreactive end caps **46** and **48**. The end cap **46** is integral with and forms part of the injector assembly. The opposite end cap **48** is provided with an outlet which is connected to a vacuum pump **50** which is adapted to maintain a negative pressure within the reaction chamber **4** at a level in the order of 1 to 50 torrs (mm. of Hg). Crystal growth is carried out in the reaction chamber on a seed crystal or another suitable substrate. In the illustrated embodiment crystal growth occurs on a seed crystal **52** which is supported by an alumina holder **54**. The latter is a solid rod held by a non-reactive wire support member **56**. The holder **54** is provided at one end with a hole into which the seed crystal **52** is force-fitted and retained by friction. Holder **54** is disposed with the seed crystal **52** exposed directly to the metal halide gas entering the chamber via the injector **42**. The flow of halide gas in the reaction chamber is essentially laminar with respect to the seed crystal. The reaction chamber **4** is surrounded by an electric resistance heater coil **58** which is connected to a separately controllable power supply (not shown) whereby it can be energized to heat the chamber to an elevated temperature. Thermocouples (not shown) are used to determine the temperature of the members heated by the electric heater coils **32**, **36**, **40**, **44** and **58**.

The outer tube of the injector operates to deliver to the reaction chamber **4** selected gases for initiating, sustaining and controlling a reaction yielding growth of a metal oxide in single crystal form. In the illustrated embodiment the outer tube is connected by a line **62** to separate lines **64**, **66**, **68** and **70** which lead to separate pressurized supply tanks **72**, **74**, **76** and **78** containing carbon monoxide, carbon dioxide, hydrogen and argon respectively. Each supply line is provided with control valves, flow meters, pressure gauges and drying tubes like the chlorine supply line **18**. The argon supply line **70** also is connected by a valve **80** to the chlorine line **18**.

Growth of metallic oxide is accomplished in the reaction chamber **4** by an overall general chemical reaction as follows:

$$aMCl_x\,(g)+bH_2\,(g)+cCO_2\,(g)\rightleftharpoons dM_yO_z\,(s)+cCO\,(g)+eHCl\,(g)$$

where *a*, *b*, *c*, *d*, *e*, *x*, *y* and *z* are whole numbers. For alumina single crystals the specific reaction is as follows:

$$2AlCl_3\,(g)+3H_2\,(g)+3CO_2\,(g)\rightleftharpoons Al_2O_3\,(s)+3CO\,(g)+6HCl\,(g)$$

It is believed to be apparent that from a theoretical standpoint it is not essential to supply carbon monoxide and argon to reaction chamber **4** in order to carry out the foregoing reaction. However in practice it has been

deemed most desirable to supply additional carbon monoxide to the system since it behaves as a reaction suppressant and thereby provides a measure of control over the reaction process. Hydrogen chloride gas also acts as a suppressant and if desired it may be supplied to the reaction chamber in place of or supplementary to the carbon monoxide additive. The argon has several functions. One function is as a diluent or carrier for the reactive gases. Its use as a diluent or carrier is optional and occurs primarily where it is desired to achieve a certain overall gas flow rate through the halide generator **2** or the reaction chamber **4** without increasing the flow rate of the reactive gases.

Under controlled temperature, pressure and concentration conditions, the stream of reactive gases will react to form and deposit a solid oxide in single crystal form directly on the seed crystal while homogeneous nucleation of solids or powder in the gas phase and formation of fibers at the surfaces of the seed crystal are essentially prevented. The growth morphology also is controlled by orientation of the seed crystal while the growth velocity is controlled by the seed orientation, the degree of supersaturation, and the temperature. At this point it is to be understood that the term "orientation" as used herein with reference to seed crystals and crystal growth of alumina or other optically uniaxial crystals which can be made by the present invention, refers to the angle included between the *c*-axis (optic axis) and the axis of growth, or principal axis of the crystal. Thus a 60° crystal is one in which its *c*-axis makes an angle of approximately 60° with its growth axis (actually 57°35′, the rhombohedral angle) while a 0° crystal is one in which the *c*-axis coincides with the growth axis. In the case of uniaxial crystals such as corundum, the direction of the *c*-axis can be determined with a polarizing microscope or by X-ray techniques. Orientation control of the crystal to be grown is achieved by seed cutting and orientation, it being well known that crystal growth of the same material on a seed crystal will tend to have the same orientation as the seed if optimum conditions of deposition and temperature are met. Accordingly, to achieve crystal growth with a 60° orientation on a given crystal which is to function as a seed, it is first necessary to determine the *c*-axis of the given crystal. With the *c*-axis determined, the seed crystal then is cut so that the *c*-axis makes the desired angle with a selected vertical axis which is to coincide with the growth axis of the crystal to be grown thereon. Using essentially the same operating conditions but changing only the seed, epitaxial growth of alpha alumina has been achieved on sapphire seeds oriented 0°, 60°, and 90°, ruby seeds oriented 60°, and polycrystalline alumina rods. Growth also has been achieved on metal substrates such as platinum and molybdenum.

Following are examples of carrying out the process according to a preferred embodiment of the present invention.

Example I

A plurality of strips of highly pure aluminum measuring .010 inch thick, 0.250 inch wide and approximately 12 inches long are placed in the halide generator **2**. A sapphire seed crystal **52** oriented 60° is mounted in holder **54** and heater **58** is energized to heat the reaction chamber **4** to a level where the seed crystal is at a temperature of approximately 1750° C. as determined by an optical pyrometer. The vacuum pump is put into operation and is allowed to establish a vacuum of less than 1 torr in the reaction chamber. Thereafter the electric heater **36** is energized so that the temperature within the halide generator is approximately 350° C. After the temperature of the halide generator has reached 350° C., chlorine is fed into the generator at the rate of 0.02 liter per minute. The temperature of the chlorine entering the halide generator is in the range of 250°–350° C. The heaters **40** and **44** are also operated so that the halide gas from the

generator 2 will be maintained at a temperature of about 275° C. as it enters reaction chamber 4.

Before introduction of chlorine gas to halide generator 2, a stream of gases consisting of hydrogen, carbon dioxide and carbon monoxide are fed to reaction chamber 4 by way of the injector 42. The hydrogen is fed at the rate of 0.16 liter per minute; the carbon dioxide at the rate of 0.04 liter per minute; and the carbon monoxide at the rate of 1.00 liter per minute. A reaction chamber pressure of approximately 10 torrs is maintained while the gases are flowing.

Almost perfectly pure $AlCl_3$ gas is produced in the halide generator 2 and, under the foregoing conditions of temperature, pressure and flow rates, this gas reacts with the hydrogen and carbon dioxide in a manner such that epitaxial vapor deposition and growth occurs on the seed crystal without concomitant whisker growth or aluminum oxide powder formation. After approximately 15 hours the process is stopped and argon gas is flushed through the reaction chamber to clean it and restore its pressure to a safe level at which it can be opened to retrieve the seed crystal. The single crystal growth on the seed 36 is found to be 60° oriented sapphire crystal and the rate of crystal growth is determined to be approximately 76.5 mg./cm.²/hr.

Example II

In this example a polycrystalline alumina rod measuring approximately ½ inch in diameter is substituted for the seed crystal 52. All other materials and conditions are the same as in Example I. The process is continued for about 17 hours. On removal from the restriction chamber it is determined that the rod has a radial overgrowth of sapphire crystals which measure up to 0.060 inch wide and 0.090 inch long.

Example III

In this example a 60° ruby crystal is inserted in the holder 54. All other materials and conditions are the same as in Examples I and II. The process is continued for approximately 10 hours. On removal from the reaction chamber the ruby seed is found to have a sapphire overgrowth with a 60° orientation. The color boundary is sharp and well defined with no observable indication of chromium diffusion from the ruby to the sapphire overgrowth. The rate of growth is approximately 90.4 mg./cm.²/hr.

Example IV

In this example a 60° ruby crystal is inserted in the holder 54. All other conditions and materials are the same as in the preceding examples except that simultaneously with the generation of $AlCl_3$ there is generated $CrCl_3$ in a generator similar to halide generator 2. The $CrCl_3$ is generated by passing chlorine gas over chromium in particle form at a temperature of approximately 350° C. and at a rate of approximately 0.0002 liter per minute. This $CrCl_3$ gas is delivered to the reaction chamber via a branch line connected to $AlCl_3$ line 38. The branch line is heated by a resistance heater coil similar to coil 40 which assists in heating the $CrCl_3$ to the temperature of the $AlCl_3$ in line 38. The process is terminated after 12 hours. On removal from the reaction chamber the seed ruby is seen to have a ruby single crystal overgrowth having an orientation of 60°.

The foregoing examples are to be considered merely illustrative of the results that can be achieved as well as the manner of growing sapphire and ruby crystals according to the present invention. Obviously the operating conditions are variable and changing one or more of these conditions will affect the rate of crystal growth. In practice growth rates of up to 90.4 mg./cm.²/hr. have been attained and seemingly the ultimate size is limited only by limitations of available apparatus. An interesting aspect of the rate of growth is that it varies according to the orientation of the seed crystal. The rate of growth increases with 90°, 0° and 60° orientation, respectively.

The rate of crystal growth is affected to an even greater extent by the flow rate and relative partial pressures of the gases supplied to the reaction chamber. In this connection it is to be noted that these gases are not supplied in true stoichiometric proportions. Instead it has been found that the optimum ratio of hydrogen to carbon dioxide is 4 to 1. Satisfactory results also have been obtained with different proportions, e.g. 10 to 1 using no carbon monoxide. It has also been determined that for best results the carbon monoxide added to the system should be supplied in the ratio of between 20 and 25 to 1 with respect to carbon dioxide when using a ratio in the order of 4:1 for hydrogen to carbon dioxide. The foregoing examples are substantially consistent with these optimum ratios. Changing the concentration of one reactant without a compensating change in the other reactants generally will change the results.

Varying the amount of carbon monoxide affects the rate of reaction. If the amount of carbon monoxide is increased, the rate of growth will be suppressed. If the carbon monoxide proportion is decreased, the rate of growth will increase but with increased chance of obtaining a polycrystalline product and extraneous alumina powder in the reaction chamber.

The pressure at which the vapor growth occurs is important. If the pressure in the reaction chamber is increased to atmospheric or near atmospheric level, single crystal formation will not result under the conditions set forth above. Instead aluminum oxide powder or whiskers or platlets will be formed. In addition, to not satisfying the objective of the invention, namely relatively large single crystal growth, the objection to obtaining aluminum oxide powder is that it is not confined to the region of the seed crystal but forms throughout the entire system where a gaseous phase exists. To avoid the formation of aluminum oxide powder it has been found that the pressure in the reaction chamber should be in the range of approximately 1–50 torrs. Above 50 torrs it is difficult to retain control of the system and aluminum oxide powder begins to form and obstructs the growth of uniform single crystals. Preferably the pressure should be below 30 torrs. In practice a pressure of 10–15 torrs is maintained in reaction chamber 4.

The rate of crystal growth is also affected by the operating temperature range within the reaction chamber. It has been found that the operating temperature range within the furnace when producing single crystals of sapphire or ruby should be in the range of 1500° C. to 1900° C. with optimum results occurring at a temperature of 1750° C. The rate of deposition increases from 1500° C. up to about 1750° C. and appears to be merely constant from that temperature up to about 1850° C. Over 1850° C. deterioration of the alumina furnace occurs. It is recognized that if the furnace were made of a material other than alumina which could withstand higher temperatures and which would not deteriorate rapidly from exposure to the gases used in the process and the surrounding air, the operating temperature could be increased above 1850° C. close to the melting point of alumina (2040° C.) and maintained at that temperature for an extended period of time. However, alumina furnaces are preferred since they are relatively cheap and possess good oxidation resistance and long life up to 1800° C. which is above the optimum operating temperature (1750° C.). Operating substantially below approximately 1500° C. is unsatisfactory. Thus if the process is carried out at a temperature in the range of approximately 1300° C. to less than 1500° C., fine single crystal whiskers or platelets result instead of relatively large size crystals.

The temperature in the halide generator may vary. As a practical matter the temperature in the halide generator must be at least above 180° C. where aluminum chloride is being produced since aluminum chloride

condenses at approximately that temperature. In practice, it is preferred that the temperature in the halide generator be in the neighborhood of 300° to 400° C. This temperature range precludes condensation of aluminum chloride at that temperature and is preferred also because the rate of reaction of the chlorine gas with the aluminum strips increases with increasing temperature.

Apart from functioning as a flushing medium for bringing the reaction chamber back to atmospheric pressure, argon may be used also as a carrier gas to control the flow rate of the aluminum chloride gas furnished to the reaction chamber. In a typical case the argon is supplied to the halide generator at a rate of 0.1 liter per minute.

To a great extent the purity of the final product is determined by the purity of the aluminum strips placed in the generator. It is preferred that the aluminum strips have a purity of 99.9+ percent. The aluminum may be in the form of strips as indicated previously or in any other form providing the exposed surface area is sufficient to permit complete reaction with chlorine.

In growing ruby crystals, it is preferred that the chromium chloride gas be generated in a separate halide generator in the manner described in Example IV. The flow of chlorine gas into the chromium chloride generator should be at a rate such that the chromium chloride gas introduced into the reaction chamber provides approximately 400 to 10,000 parts per million of chromium in the crystal grown on the seed. The rate of flow of chlorine to the chromium chloride generator specified in Example IV is designed to yield ruby overgrowth containing 400 to 500 parts per million of chromium.

While the exact reaction mechanism is not known, it is believed that the excellent results which have been obtained are due to the occurrence of a supersaturation condition in the reaction chamber. This supersaturation is believed to cause the formation of sapphire or ruby crystal atom by atom directly on the surface of the seed crystal rather than in the vapor phase. While the optimum degree of supersaturation is not known, it is believed that an increase in supersaturation will produce a corresponding increase in the rate of crystal growth, up to a maximum rate whereupon a polycrystalline product will result.

Crystals made by the process of the present invention in the manner illustrated by the foregoing examples are characterized by relatively low internal strain. This lower internal strain is inferred from dislocation density. Dislocation densities of crystals grown according to the present invention typically have an average value of approximately 10^2 dislocations per square centimeter over the entire crystal with an average of 10^4 on the basal plane (0001), in contrast to crystals grown by the Verneuil process which have been reported to have average dislocation densities ranging from 10^5 to 10^8 dislocations per square centimeter. Lower internal strain is also suggested by the absence of fused layers and lineage. Diffraction patterns obtained by Laue X-ray techniques indicate uniform single crystal structure which is confirmed by index of refraction measurements. These measurements, within the limits of precision for oil immersion techniques, indicate that crystals produced according to the present invention have refractive indices corresponding to reported values for corundum.

A further important characteristic of crystals grown by the present invention is the low impurity content. Analysis of high purity seed crystals grown by the Verneuil process and used in the growth of crystals according to the present invention has indicated a minimum to maximum total impurity content of 50 to 540 parts per million. By way of contrast, single crystal overgrowth produced as described herein has been determined to have a total impurity range of 30 to 34 parts per million. In other words the present invention makes possible single crystals which are several times purer than the crystals commonly obtained by the Verneuil process. It is believed that this lower impurity content is due at least in part to the vacuum in the reaction chamber which promotes vaporization and removal of some impurities. It also is believed that the low impurity content is due in part to the fact that gaseous reactants are used. Thus, starting the process with aluminum and chlorine and manufacturing aluminum chloride gas as an intermediate product permits better control over the purity of one of the critical reactants, i.e., the aluminum chloride gas. In this connection it is to be appreciated that attempts have been made to achieve satisfactory growth of single crystals using aluminum chloride as a starting material. However, this approach does not offer the same measure of control or purity as is possible starting with high purity aluminum. Moreover it is not economically feasible to purchase aluminum chloride in the purity demanded for the present process. What is even more important is that it is substantially impossible to control the vaporization of aluminum chloride starting material so as to avoid deposition thereof on the walls of the apparatus during the course of a run and especially after a run has been terminated. This problem does not exist when starting with aluminum strips and chlorine gas for then it is possible to quickly terminate the formation of aluminum chloride in the halide generator by cutting off the flow of chlorine. The existing vacuum exhausts substantially all of the free aluminum chloride from the system before it can deposit out on the walls of the apparatus.

As indicated earlier the invention is not limited to growth of alumina crystals such as sapphire and ruby but is applicable equally well to growth of other metal oxide single crystals. By way of example but not limitation, reactions based on the general reaction

$$a\mathrm{MCl}_x\ (g)+b\mathrm{H}_2\ (g)+c\mathrm{CO}_2\ (g)\rightleftharpoons d\mathrm{M}_y\mathrm{O}_z\ (s)+c\mathrm{CO}\ (g)+e\mathrm{HCl}\ (g)$$

(where M represents a metal and *a*, *b*, *c*, *d*, *e*, *x*, *y* and *z* are whole numbers) can be carried out according to the foregoing teachings to yield single crystals of MgO, NiO, SiO_2, TiO_2, ZrO_2, Cr_2O_3, BeO, Nb_2O_5, PbO and other single and multiple component oxides. In other words, the invention is applicable generally to the deposition of oxide crystals. In growing other kinds of crystals the same crystal purity and uniformity can be achieved since homogeneous nucleation of solids or powder in the gas phase or formation of fibers at a substrate surface can be avoided by proper control of operating conditions such as pressure, temperature and flow rates. Application of the process of this invention to other oxides is exemplified by the following example relating to the growth of SiO_2 crystals.

Example V

In this example the same apparatus is used as in Example I. However, high purity Si is placed in the halide generator instead of Al. The silicon is of the fused variety and is in lump form with the lumps having an average diameter of about ¼". An SiO_2 polycrystalline tube is mounted in holder **54** and heater **58** is energized to heat the reaction chamber **4** to a level where the tube is at a temperature of approximately 1500° C. A vacuum is established and maintained in the reaction chamber in the same manner as in Example I, being somewhat less than 1 torr at the start but kept at about 10 torrs while the reaction gases are flowing through the reaction chamber. The halide generator is heated to and kept at a temperature of approximately 350° C. After the halide generator has reached the right temperature, chlorine is supplied to it at a rate of 0.03 liter per minute. The incoming chlorine has a temperature of 250–350° C. and the $SiCl_4$ gas produced in the generator by reaction of the chlorine with the essentially pure Si is maintained at a

temperature of about 275° C. as it enters the reaction chamber.

Before introduction of the chlorine gas to the halide generator **2** a mixture of gases consisting of H_2 and CO_2 is supplied to the reaction chamber. The hydrogen is supplied at the rate of 0.80 liter per minute while the carbon dioxide is fed at a rate of 0.20 liter per minute. Under the foregoing conditions the following reaction occurs:

$$SiCl_4\ (g)+2H_2\ (g)+2CO_2\ (g)\rightleftharpoons SiO_2\ (s)+2CO\ (g)+4HCl\ (g)$$

The process is continued for five hours. On removal from the reaction chamber the tubular substrate is found to have an overgrowth of SiO_2 crystals measuring about 0.012 inch in a radial direction. Since the process reproduces the substrate, replacement of the polycrystalline tubular substrate with an SiO_2 single crystal seed will result in growth of a single crystal on the seed under the same condition.

It is to be understood that the examples, terms, and expressions which are employed in this specification are used for the purpose of description and not for the purpose of limiting or excluding equivalents and that within the scope of the appended claims, various modifications, variations, extensions, and substitutions of equivalents may be made without departing from the principles of the invention as described and illustrated.

What is claimed is:

1. A method of epitaxially growing a metal oxide in single bulk crystal form comprising the steps of providing a quantity of metal from the class consisting of Al, Ti, Si, Cr, Ni, Mg, Zr, Be, Nb and Pb, passing a halogen gas in contact with said metal at a temperature sufficient for said gas to react with said metal to form a metal halide gas, passing said metal halide gas into a chamber containing a single crystal substrate, simultaneously passing hydrogen and carbon dioxide gases into said chamber, maintaining the pressure within said chamber in the range of approximately 1 to 50 torrs, and maintaining a uniform temperature in the vicinity of said substrate within said chamber below the point of fusion of said metal oxide while sufficiently elevated to preclude formation of metal oxide whiskers and powders, in which temperature and pressure ranges the gases in said chamber react at the surface of said substrate to form a solid metal oxide overgrowth thereon of single bulk crystal form.

2. The method of claim **1** wherein the pressure is sufficiently low to prevent formation of metal oxide powder as the reaction product of said gases.

3. The method of claim **1** wherein said metal is aluminum.

4. The method of claim **1** wherein said halogen gas is chlorine.

5. The method of claim **1** wherein said metal is aluminum and said halogen gas is chlorine.

6. The method of claim **1** further including the step of feeding carbon monoxide gas into said chamber to control the rate of reaction.

7. The method of claim **1** wherein said metal is aluminum and said halogen gas is chlorine, and further including the step of passing chromium chloride gas into said chamber at a rate sufficient for said single crystal overgrowth to include chromium atoms in its lattice.

8. The method of claim **7** wherein the rate of flow of chromium chloride gas is at a rate to achieve a single crystal overgrowth containing 400 to 10,000 p.p.m. of chromium.

9. The method of epitaxially growing a single bulk crystal of synthetic corundum comprising the steps of reacting aluminum with chlorine to produce aluminum chloride gas, introducing the aluminum chloride gas together with hydrogen and carbon dioxide gases to a furnace in which is located a starting crystal of corundum,

maintaining the temperature of said reaction chamber above 1500° C. and below 2000° C. and maintaining the pressure in said furnace at a level in the range of approximately 1 to 50 torrs, whereby said gases will continually react at the surface of said starting crystal to epitaxially form a new single bulk corundum crystal.

10. The method of claim **9** further including the step of supplying a chromium halide gas to said furnace at the same time as said aluminum chloride, hydrogen and carbon dioxide gases, whereby said new single crystal of corundum will include chromium atoms in its lattice in a quantity corresponding substantially to the quantity in which chromium atoms occur in ruby crystals.

11. A method for epitaxially growing a single bulk crystal of synthetic corundum along a predetermined axis of growth comprising the steps of providing a corundum seed crystal having a predetermined *c*-axis, positioning said seed crystal in a furnace so that its *c*-axis is oriented at a selected angle to the intended axis of growth of said synthetic corundum, evacuating said furnace, heating said furnace to a temperature of at least approximately 1500° C. but below 2000° C., and continually passing into said furnace a mixture of aluminum chloride, hydrogen and carbon dioxide gases at rates sufficient to cause growth of single crystal corundum on said seed crystal.

12. The method as defined by claim **11** further including the step of feeding amember of the class consisting of carbon monoxide and hydrogen chloride gases to said furnace to control the rate of reaction.

13. The method defined by claim **11** further including the step of mixing argon gas with said gases before said gases are introduced to said furnace.

14. The method described by claim **11** wherein the flow of gases is substantially laminar in the vicinity of said seed crystal.

15. The method described by claim **11** further including the step of introducing chromium chloride gas into said furnace simultaneously with said gases, whereby the single crystal corundum newly grown on said seed crystal will contain chromium atoms in its crystal lattice.

16. The method of claim **11** wherein said hydrogen and carbon dioxide gases are in the following proportions by volume: 4 parts of hydrogen to 1 part of CO_2.

17. The method of claim **16** wherein said aluminum chloride is prepared in a halide generator by passing chlorine gas directly over pieces of highly pure aluminum at a temperature in excess of 180° C., said aluminum chloride being transported directly to said furnace as it is formed.

18. The method of claim **17** further including the step of mixing argon gas with said chlorine gas before it is introduced into said halide generator.

19. The method of epitaxially growing a metal oxide single bulk crystal comprising the steps of reacting a metal selected from the group consisting of magnesium, aluminum, chromium, nickel, silicon, titanium, zirconium, beryllium, lead and niobium with chlorine gas to yield a metal chloride gas, passing said metal chloride gas as it is formed into a furnace which contains a substrate on which said single crystal is to be grown and in which the temperature in the vicinity of said substrate is uniformly maintained below the point of fusion of said metal oxide while sufficiently elevated to preclude formation of metal oxide single crystal whiskers and in which the pressure is in the range of 1 to 50 torrs, simultaneously passing hydrogen and carbon dioxide gases into said same furnace, controlling the rates of flow of said gases whereby under the existing temperature and pressure a single crystal of a metal oxide is formed from the interaction of the gases directly at the surface of said substrate, discontinuing the generation of metal chloride gas and terminating the flow of hydrogen and carbon dioxide gases into said furnace, flushing said furnace with an inert gas to restore it to near atmospheric pressure, and thereafter removing said sub-

strate from said furnace whereby the single crystal growth thereon may be severed therefrom.

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