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**Linares**

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[54] **PROCESS OF GROWING CRYSTALS**


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[51] **Int. Cl.** ..... **B01j 17/20**

[58] **Field of Search** ..... 23/301 SP, 295; 65/99 A



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[57] **ABSTRACT**

A process of growing ionic crystals which comprises providing a support of a molten material, floating a melt of an ionic material (ionic melt) on the molten support material, the molten support material being immiscible with the ionic melt, maintaining at least a portion of the molten support material at a temperature of at least the melting point of the ionic melt, growing a crystal from the ionic melt while the ionic melt is supported on the molten support material by reducing the temperature of the ionic melt below its melting point and removing the grown crystal therefrom. In addition, this invention provides a process of eliminating anionic and cationic impurities in the ionic melt and suppressing contamination of the ionic melt by the molten support material by applying a sufficient electrical potential between the ionic melt and the molten support material. Ionic impurities are thus electrolytically removed from the ionic melt.


**12 Claims, 2 Drawing Figures**

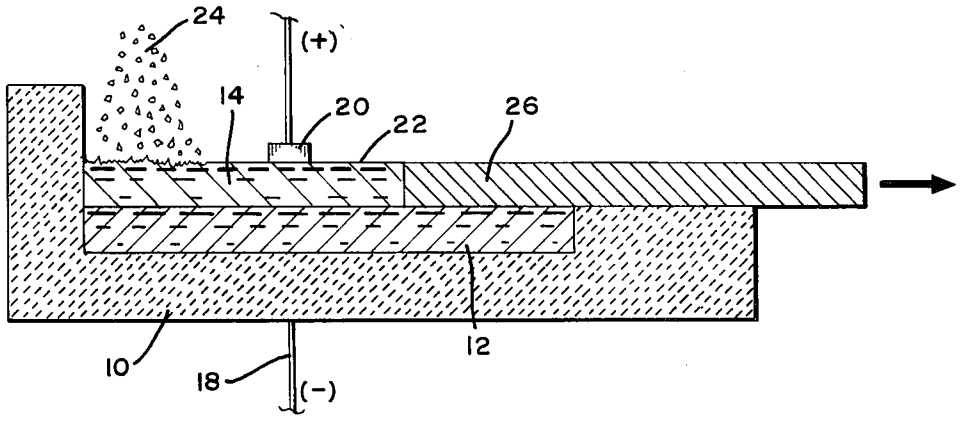


FIG. 1

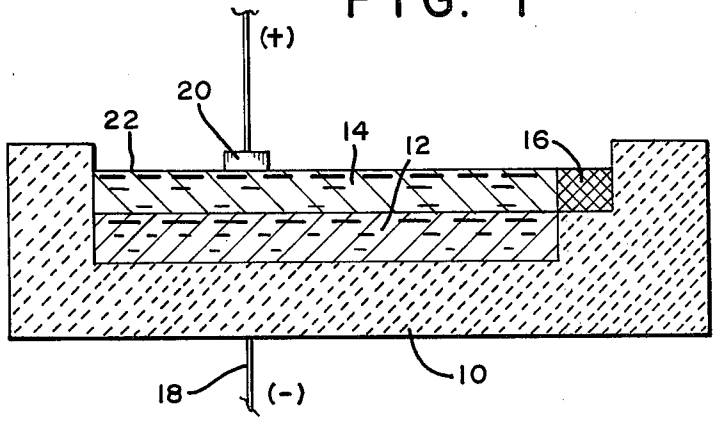
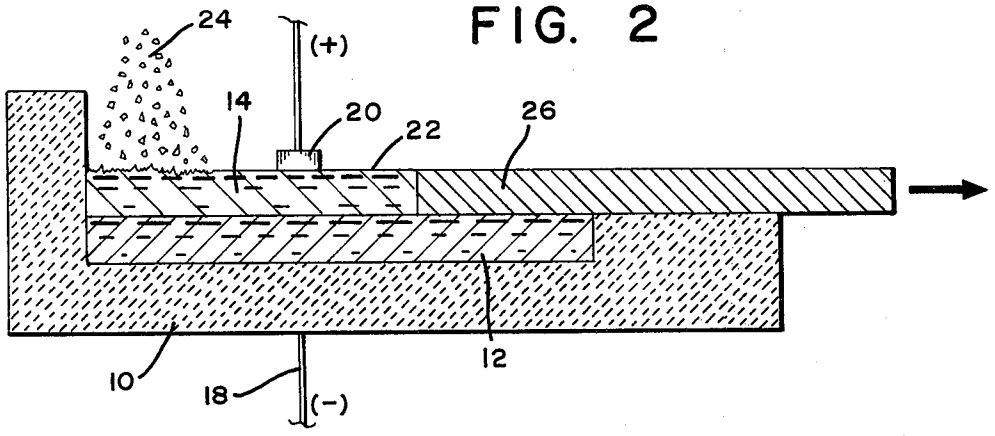



FIG. 2



# PROCESS OF GROWING CRYSTALS

## FIELD OF THE INVENTION

This invention relates to a process of growing crystals.

## DISCUSSION OF THE PRIOR ART

Within recent years, an increasingly large number of industrial and military devices have been developed which depend upon mono-crystalline components. These components include metals, semiconductors and insulators. Such crystals are useful for optical windows, lenses, gem stones, laser related devices, optical armor, as well as substrates for thin film devices and other uses.

Heretofore crystals have been grown by a variety of methods, perhaps the most widely used of which is the Czochralski method. Basically the growing technique in the Czochralski method consists of pulling a crystal rod from a molten mass of material under controlled conditions and thereafter slicing the crystals followed by grinding and lapping to obtain the precise thickness required. Usually the crystals have to be polished to provide a high degree of surface finish. Such polishing is an expensive procedure and tends to introduce surface cracks which weaken the crystal and impair its operating properties.

Some prior crystal growing methods have not been able to provide relatively thick crystals which are of acceptable purity in terms of optical, electrical, electro-optical and other properties which are required for their incorporation into the aforesaid industrial and military devices. In addition, some prior techniques introduce impurities into the crystals during the growing process. Moreover, it would be desirable to provide a process of growing crystals at lower production costs.

## SUMMARY OF THE INVENTION

In accordance with this invention a process of growing ionic crystals is provided, which process comprises providing a support of a molten material, floating a melt of an ionic material (ionic melt) on the molten support material, the molten support material being immiscible with the ionic melt, maintaining at least a portion of the molten support material at a temperature above the melting point of the ionic melt, growing a crystal from the ionic melt while the ionic melt is supported on the molten support material by reducing the temperature of the ionic melt below its melting point and removing the grown crystal therefrom. In addition, this invention provides a process of eliminating anionic and cationic impurities in the ionic melt land suppressing contamination of the ionic melt by the molten support material by applying a sufficient electrical potential between the ionic melt and the molten support material. Ionic impurities are thus electrolytically removed from the ionic melt. More particularly, in one embodiment, the process of this invention comprises producing crystals by forming a melt of an ionic material, preferably a metal halide or oxide, supporting the ionic melt on an immiscible molten material, applying an electrical potential between the ionic melt and the molten support material, solidifying the ionic melt material to thereby form an ionic crystal, supporting the crystal on the molten support material and removing the crystal from the molten support material.



## BRIEF DESCRIPTION OF THE DRAWINGS

In the drawings,

FIG. 1 is a schematic representation of a batch process for producing ionic crystals according to the present invention; and

FIG. 2 is a schematic representation of a continuous process for producing ionic crystals according to the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENT

The process of this invention may be carried out in a batch or continuous manner to grow ionic crystals in the form of bulk crystals or thin films. Single crystals as well as multicrystalline materials can be obtained. As previously mentioned, ionic crystals of various thicknesses have become increasingly important as optical crystals (e.g. as infrared windows, lenses, etc.), as substrates for thin film devices, for optical armor, and laser related devices, as well as other uses.

In accordance with my invention, a melt of an ionic material is floated or supported on a non-reactive molten support. Crystallization is controlled by imposing a lateral temperature gradient on both melts and solidification is initiated at a cold spot in the melt or at a crystal seed. The ionic melt is supported on the molten support material at least until crystal growth is complete and preferably until the temperature of the crystal is substantially reduced.

The method may be practiced as a batch or continuous process in a receptacle such as a boat or crucible. The dimensions of the crystal will be determined by the width of the molten support, by the thickness of the ionic melt and, in a continuous process, by the feed and take-off rates. Crystals having a large variety of thicknesses and sizes may be grown by this method, including bulk crystals in the form of relatively thick blocks for optical windows (e.g. about 0.1 to 6 inches thick) and thin films for use as substrates (e.g. about 0.002 to 0.10 inch thick).

The boat or crucible, which is located in a heating furnace, is suitably formed from a relatively pure, non-reactive high melting point material, such as graphite, aluminum oxide, zirconium oxide, etc. The boat is filled with a support of an immiscible molten material which is non-reactive with the ionic material (so that contamination of the crystal is minimized). The preferred molten support material is a metal, more preferably a metal which has a low vapor pressure at temperatures approximately at the melting point of the ionic material so that contamination of the crystalline material by the metal is suppressed. Examples of such supporting melt materials include tin, lead, platinum, aluminum, rhoidum, iridium, molybdenum, tantalum, gallium, copper, gold, silver, tungsten, indium, and the like.

At least a portion of the supporting melt is maintained at a temperature which is at least at the melting point of the ionic material and preferably a few degrees above such melting point. The requisite temperature may be provided by one or more electrical resistance, radio frequency or induction heaters or other heating means mounted in the furnace which surrounds the boat. The ionic material may be introduced onto the surface of the molten support material in the form of a melt or solid particulate material which thereafter

forms a melt upon contact with either the surface of the supporting melt or the previously melted ionic material.

Alternatively, the ionic material (either in molten or particulate form) may be introduced onto the surface of a solidified support material; in this case, the boat is reheated to melt the support material and the ionic material.

Crystals may be formed in accordance with this invention from ionic materials such as metal halides and refractory oxides. Examples of metal halides include alkali and alkaline earth metal halides such as sodium chloride, sodium bromide, potassium chloride, potassium bromide, strontium fluoride and barium fluoride, and the like. Examples of refractory oxides include sapphire, spinel, garnet, magnesia, beryllia, ceria, thoria, and the like.

In order to initiate crystallization, a crystal seed may be provided for contact with the ionic melt or a cold spot may be provided adjacent to the top or bottom surface of the ionic melt or on the boat at a point adjacent to the perimeter of the ionic melt. A cold spot may be provided by introducing a cooling gas at the desired initiating point, by eliminating heating elements at the desired initiating point or by other means. Generally, the initiation point is chosen to be at a location remote from the point of introduction of the ionic melt into the boat, particularly in a continuous process. A temperature gradient is maintained along a dimension of the boat (preferably the longitudinal direction in a continuous process) in a direction towards the seed or cold spot, with the temperature generally being the highest at a portion of the boat furthest removed from the initiating point and gradually decreasing across the ionic melt toward the initiating point.

In a batch process, the growth interface is gradually moved from the initiating point across the ionic melt by slowly cooling the melt to a temperature below its melting point but above that of the molten support material. The ionic melt may be cooled by reducing the temperature in the furnace (e.g. via a rheostatic control in an electrically heated furnace) or by removing the boat from the furnace. In a continuous process, it is preferred to keep the growth interface stationary with respect to the boat and move the ionic melt across the growth interface to produce the desired crystals. Preferably, a relatively constant temperature gradient across the boat is maintained and raw material is fed into the molten support material at the hotter end of the boat and crystallized material is withdrawn at the cooler end. The cooler end of the boat may be maintained by providing a cooling gas at that end, by eliminating electric heating coils at that end or by other means.

The boat is desirably surrounded by an inert atmosphere in order to reduce contamination (e.g. oxidation) of the ionic melt. For this purpose, a gas which is inert with respect to the ionic melt is employed. Preferably, the gas is also used as a cooling means to provide a cold spot for initiating crystallization in the ionic melt. When growing metal halide crystals, an inert gas such as argon, helium, neon, etc. is utilized. When growing refractory oxide crystals, the inert atmosphere may be provided by the above-mentioned inert gases or by air.

During crystal growth, the crystal is supported by the molten support material. The crystal is thereafter removed in a suitable manner. In a batch process, this may be done by draining the molten support material through a drain plug, etc. and then removing the crystal from the boat; the boat may then be cooled to room temperature before the crystal is removed therefrom. Alternatively, the crystal can be removed directly from the molten support material. In a continuous process, the ionic material preferably is continuously removed from the supporting material as a continuous crystal in either the form of a thin continuous film or a continuous bulk crystal after growth is complete.

Incorporation of impurities from molten support materials such as liquid metal substrates can be suppressed by placing a small electric field between the floating ionic melt and the liquid metal substrate. The voltage applied in the field is lower than the decomposition voltage of the ionic melt at its elevated temperature and is chosen to be intermediate between the oxidation potentials, measured at the melting point of the ionic material, of the metallic constituent of the ionic melt and the supporting material. For this purpose, an electrode may be included on the surface of the ionic melt or inserted into the melt and is electrically connected as an anode. The electrode, which may be formed from, for example, graphite, iridium, platinum, etc., may be conveniently floated on the ionic melt surface. The molten support material is electrically connected as a cathode; this may be achieved, for example, by connecting the boat (which is in contact with the molten support material) as a cathode. The portion of the boat which is in contact with the ionic melt should in some cases be electrically insulated from the ionic melt. By providing the ionic melt as anode and the molten support material as cathode and applying the requisite voltage, the tendency for the molten support material to be incorporated into the ionic melt (and hence in the ionic crystal) will be suppressed. Additionally, cationic impurities in the ionic melt will tend to be electro-deposited onto the support material while anionic impurities will tend to be drawn to the anode. In many instances, the anionic impurities will be in gaseous form at the anode and will be released from the ionic melt at its interface with the surrounding gaseous medium. As a result, crystals of high purity can be obtained. The anode is preferably removed from the ionic melt before crystallization is initiated. However, the anode may alternatively remain in contact with the ionic melt during crystallization of a portion of the melt in order to provide crystals of higher purity. In some cases, it may be desirable to retain the anode in contact with the ionic melt during the entire crystallization process so that the anode is embedded in the ionic crystal.

It should be apparent that the invention provides an economical way of producing high quality ionic crystals for several reasons. In many cases, it may be possible to dispense with finishing the surface of the crystal which was in contact with the molten support material since such surface will be atomatically smooth. Moreover, crystals may be continuously grown. In addition, by being able to electrolytically remove ionic impurities from the ionic melt, raw materials of lower purity and expense can be utilized in the process.

With reference to the drawings, wherein like numerals refer to like parts, there is shown in FIG. 1 in schematic form a batch process for producing ionic crystals in which a boat or crucible **10** supports a molten support material **12**, which in turn supports a molten ionic

material (ionic melt) **14.** Boat **10** is suitably heated by means not shown. Ionic melt **14** may be provided on support material **12** by any suitable manner disclosed above. A crystal seed or cold spot **16,** which is in contact with ionic melt **14,** is provided on one end or side of boat **10.** It should be understood, of course, that a seed or cold spot may be in contact with the upper or lower surface of the ionic melt. Boat **10** is electrically connected via connection **18** as cathode; thus the molten support material **12** which is in contact with boat **10** is also a cathode. Boat **10** may be electrically insulated from ionic melt **14** by means not shown. Electrode **20** is floated on surface **22** of ionic melt **14** which interfaces with a gaseous medium and is electrically connected as an anode. An electrical potential is applied between electrode **20** and connector **18.**

FIG. **2** depicts in schematic form a continuous process for producing ionic crystals which is similar to the batch process shown in FIG. **1.** Ionic material **24** is shown as being continuously fed in particulate form to provide a continuous supply of ionic melt **14** on molten support **12** and the grown ionic crystal **26** is continuously removed from molten supporting material **12** in a direction indicated by the arrow. As in FIG. **1,** heating means for boat **10** are not illustrated.

The following are examples of the process of this invention.

## EXAMPLE I

### Growth of Sodium Chloride Crystals

**1118** Grams of tin are heated to 300°C. in a rectangular graphite crucible located in a furnace provided with electrical resistance heaters. The crucible is provided with a drain plug. Argon gas, introduced at room temperature at one end of the furnace, is passed over the crucible at a flow rate of about 500 cc/minute (ccm) to provide an inert atmosphere and also as a cooling means. The furnace is turned off and the tin is allowed to cool to room temperature. 346 Grams of granular sodium chloride are placed on top of the solidified tin layer and the crucible is heated to 830°C. With the argon flow rate maintained at 500 ccm, the crucible is then slowly cooled at 5° per hour until a temperature of 780°C. is reached and then cooled at 100° per hour until a temperature of 300°C. is reached. The rate of cooling is controlled by rheostatically reducing the electrical input to the heater. The molten tin is then drained from the crucible by removing the drain plug and the crucible is cooled to room temperature. A sodium chloride crystal ingot having an approximate size of 4 inches square by one-half inch thick is removed from the crucible.

## EXAMPLE II

### GROWTH OF SAPPHIRE CRYSTALS

50 Grams of platinum are heated to 200°C. in a cylindrical zirconium oxide crucible located in an electrically heated furnace in the presence of air. The molten platinum surface is covered with 0.75 grams of sapphire powder and the temperature is increased to 2100°C. The crucible is slowly cooled to 1900°C. by reducing the electrical input to the furnace. A solidified multicrystalline sapphire film having approximate dimensions of ¼ inch diameter and 0.010 inch thickness is removed from the crucible with a sapphire rod.

## EXAMPLE III

### Growth and Electrolytic Purification of Potassium Chloride Crystals

50 Grams of tin are heated to 250°C. in a cylindrical graphite crucible in the presence of argon. The crucible is located in a furnace provided with radio frequency heaters. Argon gas is introduced at one end of the furnace at room temperature and at a flow rate of 100 ccm. The molten tin surface is covered with 50 grams of granular potassium chloride and the crucible is heated to 800°C. A carbon electrode (anode) is inserted into the potassium chloride melt and an electrode (cathode) is attached to the crucible. The potassium chloride melt is electrolytically purified by applying 1.0 volt of direct current between the anode and cathode for 30 minutes. The anode is then removed from the ionic melt and the crucible is cooled to room temperature. A potassium chloride crystal ingot having approximate dimensions of 2 inches diameter and one-fourth inch thickness is removed from the crucible. Analysis of the crystal shows impurity levels of 0.7 ppm tin and 0.3 ppm lead. The granular potassium chloride starting material has impurity levels of 9 ppm tin and 50 ppm lead.

## EXAMPLE IV

### Continuous Growth of Sodium Chloride Crystals

A quantity of tin is melted in a rectangular crucible located in a furnace provided with electrical resistance heaters. The heaters are so arranged that one end of the tin support (hot end) is maintained at 830°C. and the other end (cold end) is maintained at 300°C. A lateral thermal gradient of 3°C. per centimeter is imposed on the molten tin. Argon gas is continuously introduced at room temperature at one end of the furnace and is continuously passed over the crucible at a flow rate of about 500 ccm. Particulate sodium chloride is continuously introduced onto the molten tin at the hot end and is melted on the surface of the tin. A bulk single crystal of about one-half inch thickness is continuously grown and is supported by the molten tin until the crystal has been cooled to 300°C. The crystal is continuously removed from the cold end of the tin at a take-off rate of 2 inches per hour.

It is to be understood that variations and modifications of the present invention may be made without departing from the spirit of the invention. It is also to be understood that the scope of the invention is not to be interpreted as limited to the specific embodiment disclosed herein, but only in accordance with the appended claims when read in the light of the foregoing disclosure.

I claim:

**1.** A process for growing ionic crystals comprising

a. providing a molten support comprising a metal selected from the group consisting of tin, lead, platinum, aluminum, rhodium, iridium, molybdenum, tantalum, gallium, copper, gold, silver, tungsten and indium,

b. floating a melt of an ionic material selected from the group consisting of refractory oxides on said molten support, said molten support being immiscible with said ionic material,

c. maintaining at least a portion of said molten support at a temperature of at least the melting point of said ionic material,

d. growing a crystal from said ionic molten material while said material is supported on said molten support by reducing the temperature of said ionic molten material below its melting point, and

e. removing the grown crystal from said molten support.

**2.** A process as claimed in claim **1** wherein said ionic material is selected from the group consisting of sapphire, spinel, garnet, magnesia, beryllia, ceria and thoria.

**3.** A process as claimed in claim **1** including initiating growth of said crystal at a cold spot in said molten ionic material.

**4.** A process as claimed in claim **1** including introducing the ionic molten material onto said molten support at a first location, initiating crystallization at a point removed from said first location, and maintaining a temperature gradient along a dimension of the ionic molten material in a direction towards said initiating point, such that the temperature is highest adjacent said first location and gradually decreases across the ionic molten material towards said initiating point.

**5.** A process as claimed in claim **1** including applying an electrical potential between said ionic molten material and said molten support to remove impurities from said ionic molten material and suppress contamination of said ionic molten material by said molten support.

**6.** A process as claimed in claim **5** wherein said electrical potential is at a value between the oxidation potentials, measured at the melting point of said ionic material, of the constituents of said ionic material and said molten support.

**7.** A process as claimed in claim **1** including continuously floating said ionic molten material on said molten support, continuously solidifying said ionic molten material to form an ionic crystal, and continuously removing said crystal from said molten support.

**8.** A process as claimed in claim **7** including continuously applying an electrical potential between said ionic molten material and said molten support to continuously remove impurities from said ionic molten material and suppress contamination of said ionic molten material by said molten support.

**9.** A process as claimed in claim **1** including initiating growth of said crystals on a crystal seed.

**10.** A process for growing ionic crystals comprising

a. providing a molten support,

b. floating a melt of an ionic material on said molten support, said molten support being immiscible with said ionic material,

c. maintaining at least a portion of said molten support at a temperature of at least the melting point of said ionic material,

d. applying an electrical potential between said ionic molten material and said molten support to remove impurities from said ionic molten material and suppress contamination of said ionic molten material by said molten support,

e. growing a crystal from said ionic molten material while said material is supported on said molten support by reducing the temperature of said ionic molten material below its melting point, and

f. removing the grown crystal from said molten support.

**11.** A process as claimed in claim **10** wherein said electrical potential is at a value between the oxidation potentials, measured at the melting point of said ionic material, of the constituents of said ionic material and said molten support.

**12.** A process as claimed in claim **11** wherein said ionic molten material is a refractory oxide.

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