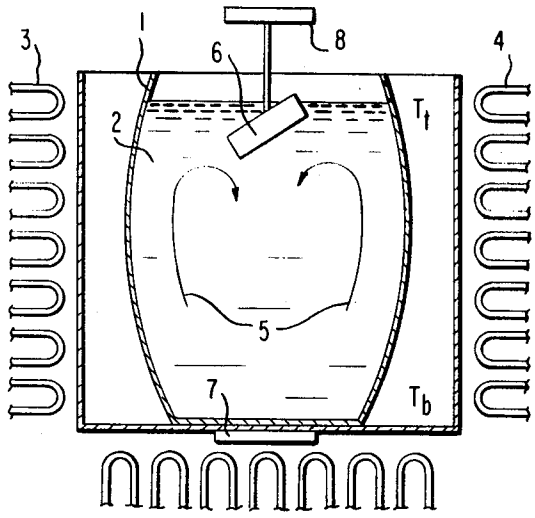
July 18, 1972 W. N. LAWLESS 3,677,718

TECHNIQUE FOR FLUX GROWTH OF BARIUM TITANATE SINGLE CRYSTALS

Filed May 5, 1969 3 Sheets-Sheet 1

FIG. 1



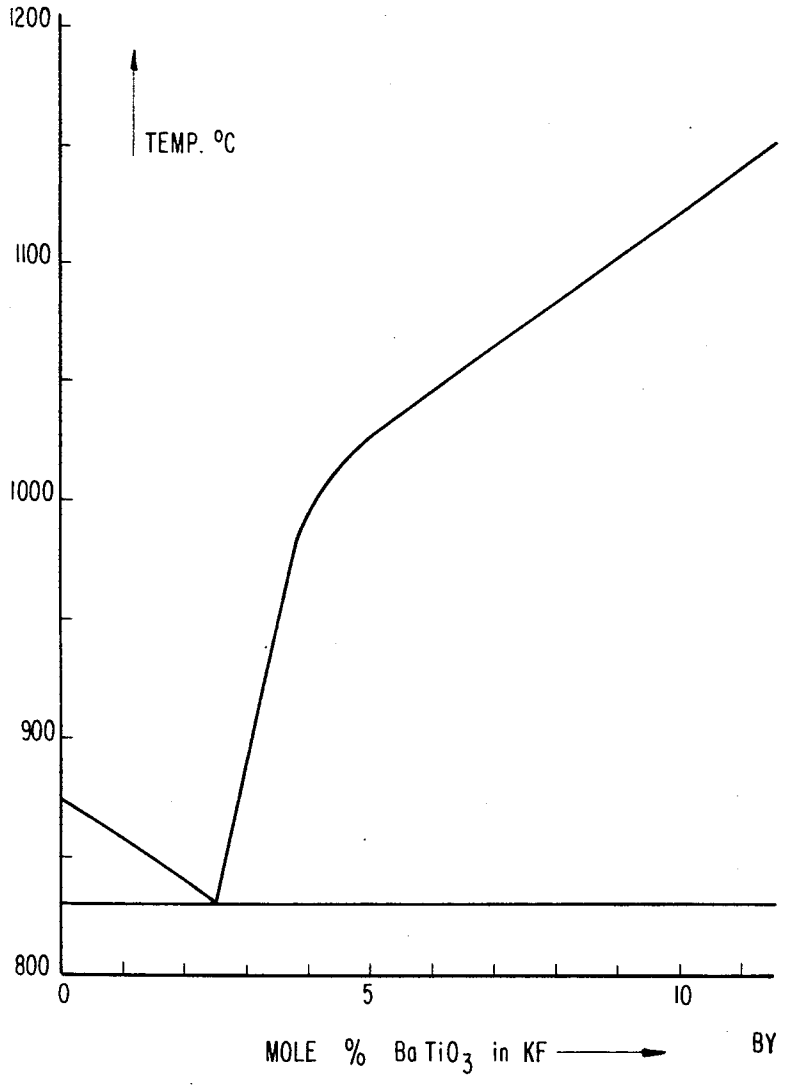


FIG. 2

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TECHNIQUE FOR FLUX GROWTH OF BARIUM TITANATE SINGLE CRYSTALS

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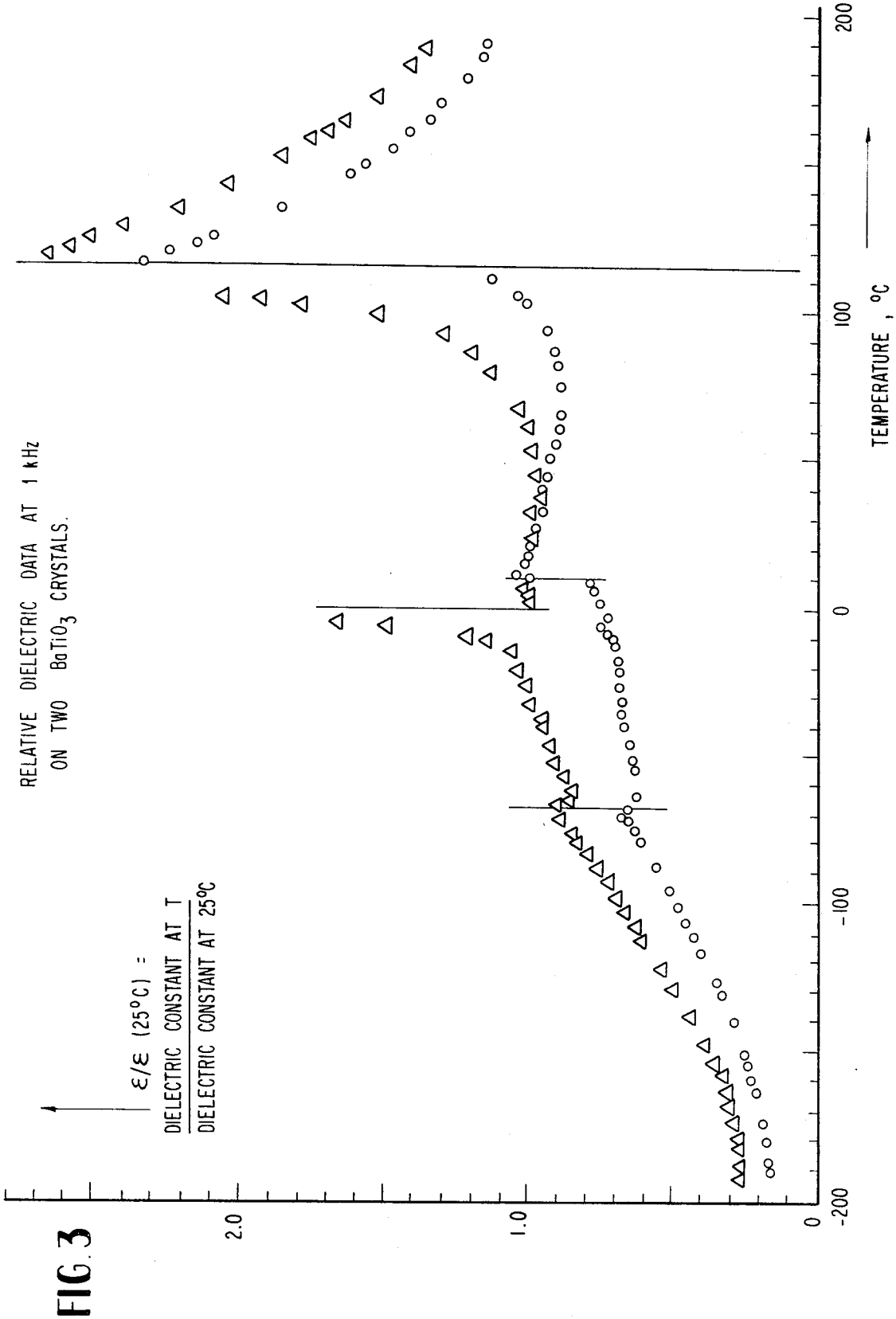


FIG. 3

TECHNIQUE FOR FLUX GROWTH OF BARIUM TITANATE SINGLE CRYSTALS

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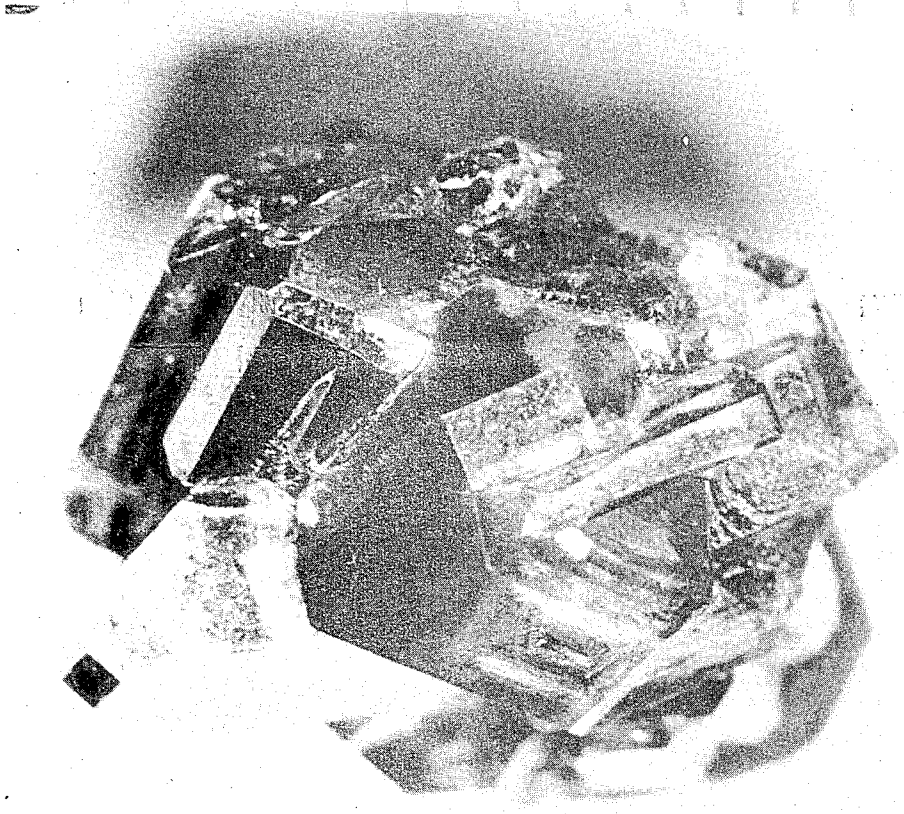


FIG. 4

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TECHNIQUE FOR FLUX GROWTH OF BARIUM TITANATE SINGLE CRYSTALS

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Int. Cl. C01f 11/00; B01j 17/04
U.S. Cl. 23—301 R 8 Claims

ABSTRACT OF THE DISCLOSURE

Process for the growth of large, thick barium titanate single crystals by heating a flux containing barium titanate, inserting therein barium titanate seed crystals, cooling the mixture to crystallize barium titanate single crystals, while maintaining a temperature gradient across the mixture and removing the grown barium titanate single crystals. The crystals formed by the above process find particular usage in optical devices.

BACKGROUND OF THE INVENTION

Field of the invention

The present invention relates to a process for the growth of large, thick barium titanate single crystals.

Description of the prior art

Barium titanate is a well known ferroelectric material which, in its ordinary flat crystalline form, is especially adapted for use in memory devices by virtue of its rectangular hysteresis loop characteristic. However, it is particularly desirable to employ large, thick barium titanate single crystals having a cubic habit when utilizing the material for its dielectric and optical properties.

Previously proposed processes for preparing barium titanate crystals, however, generally result in the formation of crystals of widely varying habit which are small and extremely thin. The process most commonly employed comprises admixing predetermined percentages of barium titanate and flux material, e.g., potassium fluoride, and heating or soaking the resulting mixture until it attains a liquid state. Sufficient quantities of barium titanate are employed such that an excess will remain in the mixture after the soaking process to act as seed crystals. The mixture is then cooled to the crystallization temperature whereupon barium titanate crystals are produced.

The process is normally carried out in a heat resistant crucible wherein the crystals are grown at the lower portions of the crucible or at the bottom of the contained mixture. Upon completion of crystal growth, the remaining flux is either decanted at a temperature above the melting point or is allowed to solidify around the crystals and subsequently washed away with a suitable solvent.

The crystals grown by this process are the so-called twin or butterfly crystals. They generally comprise a formation of two right triangle plates joined at their hypotenuses at an angle of approximately 39°. These so-called butterfly crystals are characteristically small and extremely thin. Generally, their thicknesses average approximately 0.2 millimeter. In addition, they are extremely difficult, if not totally impossible, to dope homogeneously.

It is extremely difficult to decant the extremely hot molten flux material from the crystals. If the flux material is solidified around the grown crystals, the dissolution of the solidified flux by washing with a solvent such as water, becomes a somewhat expensive and time consuming process.

The employment of excess amounts of barium titanate

in order to insure the presence of seed material extends the time necessary to effect dissolution of the barium titanate in the flux material. Also, the barium titanate collects as a solid material at the bottom of the crucible containing the molten flux material. Thereafter, the dissolving action proceeds at an even slower rate since the barium titanate can dissolve into the flux material only from the upper surfaces of the collected barium titanate material at the bottom of the crucible in contact with the molten flux.

Thus, it is apparent that the prior art processes suffer from several disadvantages. First, they are productive or small, thin barium titanate crystals having an undesirable structure and configuration rendering them inferior for use as a ferroelectric material for optical purposes. Secondly, the barium titanate crystals produced by the prior art processes have proven to be very difficult to homogeneously dope.

It is an object of the present invention, therefore, to provide an improved process for the formation of large, thick barium titanate single crystals in a pure state having improved ferroelectric properties, especially for usage in electro-optic light modulating devices.

It is a further object of the present invention to provide a process for the formation of barium titanate single crystals wherein flux decantation or solvent removal of solidified flux is unnecessary.

It is another object of the present invention to provide a process for the formation of barium titanate single crystals which can easily be homogeneously doped.

SUMMARY OF THE INVENTION

The process of the present invention achieves these and other objects by soaking a barium titanate-flux mixture in a suitable container while maintaining a temperature gradient across the mixture thereby promoting convection currents in the liquefied flux. A barium titanate seed crystal containing support is positioned in the melt in such a manner that the convection currents continuously permeate the mixture, carrying dissolved barium titanate from the hotter portion to the supported seed crystals at the cooler portion for crystallization. The crystals formed on the support are separated from the liquefied flux by merely withdrawing the support and allowing the liquid flux to drain off from the crystals.

It has been found that this process results in the formation of large, thick single crystals of barium titanate having a cubic habit rather than the thin butterfly plates produced by the typical prior art processes. The new single crystals of this invention find particular application in optical devices, such as electro-optic light modulating devices. The prior art "thin" crystals, while suitable for use in memory devices (as are the crystals of the present invention) are not completely suitable for use in optical devices, such as a light modulator. The maintenance of a temperature gradient across the flux mixture enhances mass transport within the mixture. The optimum temperature gradient has been found to be 20–30° C./inch of melt. Thus, the dissolved barium titanate in the molten mixture is continuously carried to the crystallization zone, thereby hastening the crystallization process and resulting in the formation of large, thick crystals. Moreover, the agitation in the flux mixture due to these convection currents enhances the dissolution rate of the undissolved barium titanate in the flux material during the soaking step.

The positioning of the crystals in the molten flux also obviates the necessity for insuring that undissolved barium titanate be present in the flux during crystal growth. Moreover, the necessity of a decantation step or the washing away of solidified flux is obviated. In order to obtain

pure crystals during the process of the present invention, it is only necessary to raise the seed holder support from the flux and allow the liquefied flux to drain away from the grown crystals.

It is apparent, therefore, that the process of the present invention obviates many of the disadvantages associated with the typical prior art processes.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates apparatus suitable for carrying out the process of the invention.

FIG. 2 is a phase diagram for a barium titanate-potassium fluoride system.

FIG. 3 is a plot of the change in the dielectric constant of two barium titanate crystals at various temperatures.

FIG. 4 is a photo-micrograph illustrating a top-seeded, flux-grown barium titanate crystal formed by the process of this invention.

DETAILED DESCRIPTION OF THE INVENTION

The invention is further illustrated by reference to the accompanying drawing wherein:

FIG. 1 illustrates apparatus suitable for carrying out the process of the invention, and

FIG. 2 is a phase diagram for a barium titanate-potassium fluoride system.

FIG. 3 is a plot of the change in the dielectric constant of two barium titanate crystals at various temperatures.

FIG. 4 is a photo-micrograph illustrating a top-seeded, flux-grown barium titanate crystal formed by the process of this invention.

In FIG. 1, crucible **1** substantially completely filled with a barium titanate-potassium fluoride flux mixture or melt **2** is heated in gradient furnace **3**. Gradient furnace **3** contains heating elements **4** capable of producing different temperatures in the various sections within the furnace **3**. By maintaining the temperature at the bottom of the crucible T_b higher than the temperature at the top of the crucible T_t a temperature gradient is maintained across the mixture or melt **2**. The temperature gradient created by the difference $(T_b - T_t)$ sets up convection currents **5** in the melt **2** due to the hot portions of the melt at the bottom rising and the cooler portions of the melt at the top descending.

A barium titanate seed crystal containing platform or support **6** is movably positioned within crucible **1** in such a manner that it may be lowered into or raised out of melt **2**. Alternatively, seed holder platform **6** may be held stationary and crucible **1** movably positioned with respect to the platform.

In a preferred embodiment, thermocouples **7** and **8** are positioned at the bottom and top of the crucible, respectively, for measuring and controlling the temperature at these areas.

It is preferred, though not necessary, to employ a barrel-shaped crucible, i.e., a container having a wider cross section at the middle than at the top and bottom portions thereof, as shown in FIG. 1. It has been found that this container shape provides virtually stagnation-zone-free melts. Stagnation zones may be defined as regions in the melt wherein no movement of the melt takes place thereby giving rise to extensive irregular crystallization of the undesired type of barium titanate crystals in these areas, thereby reducing the yield of the desirable single crystal barium titanate having a cubic habit. It has been found that a barrel-shaped crucible substantially coincides with the envelope of the convection currents created by the temperature gradient $T_b - T_t$. Thus, the convection currents completely permeate the entire mixture or melt thereby reducing the number of stagnation-zones.

Any furnace or heating means capable of creating a temperature gradient across the melt may be employed. The crucible containing the melt may be placed on the surface of a heating element and insulating means provided to insure that the requisite temperature gradient is maintained across the melt. However, it is preferred to employ a gradient furnace wherein each individual section thereof is subject to strict temperature control. The crucible may be constructed of any heat resistant material which is inert with respect to the melt materials. Platinum is a preferred material of construction. Likewise, the seed holder support or platform may be constructed of any heat resistant, inert material, such as platinum.

Potassium fluoride has been found to be an excellent flux material for the production of barium titanate single crystals. Conceivably, any concentration of barium titanate in the potassium fluoride flux may be employed. As a practical matter, however, the concentration of barium titanate in potassium fluoride is generally maintained below about 15 mol percent, preferably between 4½ and 6 mol percent of barium titanate. The reason for this is that higher concentrations of barium titanate require longer soaking times and higher soaking temperatures which would result in increased evaporation of potassium fluoride and possible thermal damage to the crucible, seed holder platform, etc. It has been found that concentrations of 4½ and 6 mol percent barium titanate require soaking temperatures of at least 1025° C. and 1050° C. respectively. Generally, temperatures up to about 1200° C. may be employed during the soaking step without risking the loss of excessive amounts of potassium fluoride through evaporation. The parameters which define the soaking time are: (1) that the time be long enough to insure dissolution; and (2) that the time be short enough to avoid excessive evaporation. For instance a soaking time of 2 hours may be taken as representative.

It is critical to the practice of the invention that a temperature gradient be maintained across the barium titanate-potassium fluoride melt such that the upper portions of the mixture are cooler than the lower portions. As a result, convection currents are set up in the melt in such a manner that the hottest portions of the melt are constantly rising to the cooler zones at the top of the crucible while the cooler portions of the melt are constantly descending to the hotter sections of the crucible at the bottom. It is also essential to the practice of the invention that the seed crystals be positioned in the cooler upper portions of the melt during the crystal growth period. Of course, the upper portion of the melt must also be maintained at a temperature greater than the liquidus of the composition. As a result, dissolved barium titanate is constantly being supplied to the growing seed crystals by the above described convection current, thereby giving rise to the rapid production of large, thick single crystals of barium titanate having a cubic habit.

The system must further be in equilibrium before the seed crystals are introduced into the melt.

Generally, a temperature gradient of from about 20° to about 30° C. per inch of barium titanate-potassium fluoride melt is maintained across the mixture. It is to be understood, however, that any temperature gradient capable of promoting convection currents in the mixture which are of a degree sufficient to yield good quality crystals may be employed. It has been found, however, that when the temperature gradient was narrowed to 10° C., or increased to 40° C., per inch, inferior crystals resulted.

The process of the invention as carried out using the apparatus depicted in FIG. 1 will be described by the following non-limiting example.

EXAMPLE

A platinum crucible 5 inches in height was substantially completely filled with a mixture of 6 mol percent barium titanate in potassium fluoride. Both the barium titanate and the potassium fluoride were initially mixed in the form of powders. The crucible was placed in a gradient furnace in such a manner that the temperature at the bottom of the crucible T_b was maintained at 1180° C. and the temperature at the top of the crucible T_t was

maintained at 1070° C. Thus, a hot-to-cold vertical temperature gradient was established. The mixture was heated until completion of the melting process was indicated by the stabilization of the thermocouple EMF at the bottom of the crucible. The melt was permitted to soak for one additional hour at a T_b of 1180° C. to insure equilibrium. It is necessary that equilibrium be established in the system prior to the introduction of the seed crystals. The temperature gradient $T_b - T_t$ resulted in convection currents being set up in the melt and a completion of the melting and dissolution process within a short period of time. The barrel shape of the crucible insured that all areas of the melt were agitated by the convection currents. If desired, a lid may be utilized to minimize potassium fluoride evaporation loss while allowing vertical motion of the seed crystals. In this particular example, C.P. grade barium titanate and analytical grade potassium fluoride were utilized.

Referring now to FIG. 2 which represents a phase diagram of barium titanate-potassium fluoride mixtures, it can be seen that a melt of 6 mol percent of barium titanate in potassium fluoride reaches a solidus upon being cooled to 1050° C. and a eutectic at 830° C.

Accordingly, T_b was lowered at a rate of 4° C. per hour while maintaining the same temperature gradient until T_t reached 1050° C. A platinum support connected to a thermocouple and containing barium titanate seed crystals was lowered into the melt and positioned 0.25 inch below the surface of the melt. By monitoring T_t through the thermocouple, the exact temperature at which the seed crystal touches the melt can be determined. Cooling was continued at a rate of 4° C. per hour while maintaining the same temperature gradient to insure that all of the dissolved barium titanate came into contact with the seed crystals by virtue of being agitated by the convection currents. Crystal growth was contained until T_t reached 850° C., i.e., just above the eutectic. The platform containing the grown crystals was raised out of the melt and the molten potassium fluoride allowed to drain off of the crystals.

The total "growth" period was about 50 hours in the present example.

As easily identifiable parameters, after the charge is molten and the furnace has cooled, the seed may be lowered onto the melt surface when the surface reaches the liquidus with a thermocouple in the seed rod being utilized to monitor this step. Further, the seed rod may be withdrawn when the temperature at the bottom of the crucible is at a point just above the liquidus.

A cluster of large, thick barium titanate crystals having a cubic habit with well developed faces was obtained. The average size of the crystals was about 8 millimeters by 3 millimeters by 3 millimeters. No additional purification of the crystals was required.

To further amplify upon the present invention, both single crystals and sintered discs of barium titanate can be utilized as the seed material. Although the crystals obtained in the present example measured 8 x 3 x 3 mm., the crystals are often cubic in form, having a size of 2–5 mm. on edge.

It is to be understood that by the term "soaking" is meant the steps of heating the barium titanate and potassium fluoride mixture to effect melting and dissolution and the further heating to attain equilibrium conditions.

It is to be further understood that T_b and T_t may be varied according to any particular set of circumstances. It is only necessary that T_b be higher than T_t, that T_t be above the solidus of the mixture during the soaking step and that $T_b - T_t$, i.e., the temperature gradient, be sufficient to promote convection currents in the melt.

Although any desired cooling rate may be employed for the crystal growth, a cooling rate of between 1° and 5° C. per hour has been found especially satisfactory.

It should also be understood that the mixture need only be cooled to a temperature sufficient to promote crystallization of barium titanate at the upper portion of the crucible, i.e., that area containing the seed crystals suspended in the mixture. The remainder of the mixture need not be so cooled, and, in fact, nucleation at the bottom portion of the crucible should be avoided.

It is to be further understood that the seed crystals employed should correspond in crystal structure to those produced by the process, namely, single crystals having a cubic habit.

As will be apparent to persons skilled in the art, various modifications and adaptations of the process described will become readily apparent without departure from the spirit and scope of the invention, the scope of which is defined in the appended claims.

I claim:

1. A process for the preparation of large, thick barium titanate single crystals having a cubic habit comprising: (a) soaking a mixture of barium titanate and a flux material which is potassium fluoride at an elevated temperature above the liquidus, (b) maintaining a temperature gradient across said mixture such that the upper portion of said mixture is cooler than the lower portion, said temperature gradient being sufficient to promote convection currents in said mixture, (c) cooling said mixture to a temperature sufficient to promote crystallization of barium titanate in the upper portion of said mixture, (d) positioning externally supported barium titanate seed crystals in said upper portion of said mixture during said cooling step while maintaining said temperature gradient across said mixture whereby large, thick barium titanate single crystals having a cubic habit are grown and (e) withdrawing said single crystals from said mixture.

2. The process of claim 1 including allowing excess flux material to drain off from said single crystals.

3. The process of claim 1 carried out in a barrel-shaped crucible substantially completely filled with said mixture whereby said convection currents substantially completely permeate said mixture.

4. The process of claim 1 wherein said mixture contains up to about 15 mol percent barium titanate.

5. The process of claim 1 wherein said mixture contains from about 4½ to about 6 mol percent of barium titanate.

6. The process of claim 1 wherein said mixture is soaked at a temperature of from about the liquidus of said mixture to about 1200° C.

7. The process of claim 1 wherein a temperature gradient of from about 20° to about 30° C. per inch is maintained across said mixture.

8. A process for the preparation of large, thick barium titanate single crystals having a cubic habit consisting essentially of the sequential steps of: (a) substantially completely filling a barrel-shaped crucible with a mixture of about 6 mol percent of barium titanate in potassium fluoride, (b) soaking said mixture in a gradient furnace at an elevated temperature above the liquidus while maintaining a temperature gradient across said mixture such that the temperature of the lower portion of said mixture at the bottom of said crucible is about 1180° C. and the temperature of the upper portion of said mixture at the top of said crucible is about 1070° C., said temperature gradient being from about 20° C. to about 30° C. per inch whereby convection currents are promoted in said mixture which substantially completely permeate substantially all of said mixture, (c) gradually cooling said mixture at a rate of from about 1° to about 5° C. per hour while maintaining said temperature gradient until the temperature of the upper portion of said mixture reaches about 1050° C., (d) positioning externally supported barium titanate seed crystals in said upper portion of said mixture, (e) continuing to cool said mixture at a rate of about 4° C. per hour until the temperature of the upper portion of said mixture reaches about 850° C. while maintaining said temperature gradient whereby large, thick single crystals of barium titanate having a cubic habit are grown on said

support, (f) withdrawing said support containing said single crystals of barium titanate from said mixture, (g) allowing excess potassium fluoride to drain off from said single crystals and (h) removing said single crystals from said support.

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