Jan. 21, 1947. C. D. WEST 2,414,679

PROCESS OF CRYSTAL FORMATION

Filed Sept. 14, 1944

FIG. 1

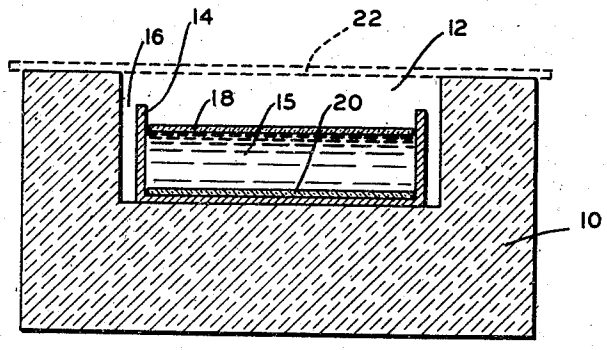
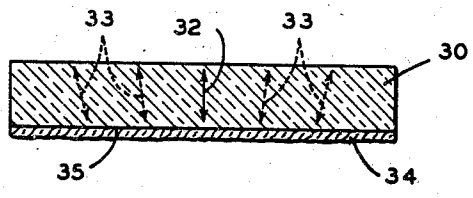


FIG. 2



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PROCESS OF CRYSTAL FORMATION

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11 Claims. (Cl. 23—302)

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This invention relates to crystallography and more particularly to a new process for producing single crystals of predetermined size and orientation. This application is a continuation-in-part of my copending joint application with Frederick J. Binda, Serial No. 547,263, filed July 29, 1944.

In said application there is disclosed a process for growing relatively large single crystals of uniaxial material and particularly basal sections of uniaxial crystals such as sodium nitrate. In general, said process comprises forming a melt comprising the desired crystalline material, bringing into contact with said melt a single crystal of a material substantially infusible at the temperature of the melt, substantially insoluble in said melt, separable from a formed crystal and different than said melt, said second-named crystal having a plane surface thereof in contact with said melt and having said surface extending over at least a greater part of the cross-sectional area of the melt, said surface substantially defining the desired cross-sectional area of the said crystal to be formed, said crystal surface having an atomic structure capable of drawing out of the melt and holding a monatomic layer of atoms in a predetermined network having the same geometry as, and substantially the same size as, a like atomic network in the final formed crystal. Said application discloses the use of a cleavage section of mica as an example of a particularly suitable material for influencing the growth of the new crystal. It is further disclosed in said application that the mica may be floated on the top of the melt and the new crystal grown from the top down, or that the mica may be positioned at the bottom of the melt and the melt crystallized from the bottom.

Excellent results have been obtained with the process shown in said application from the standpoint of producing large basal sections of sodium nitrate and mixed crystals containing sodium nitrate. In practicing said process for quantity production, however, it has been found that there is a tendency in the new crystals for the optic axis to fail to remain perpendicular to a plane over the whole area of the crystal but rather to wander so as to be substantially perpendicular to an approximately spherical or cylindrical surface of a relatively large radius of curvature, said surface being convex on the side of the crystal adjacent the mica. This in turn creates problems of parallax when the crystal is viewed in polarized light. For example, if such a basal section is mounted between circular polarizers there is visible therein an interference pattern

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at infinity comprising a series of concentric rings, but said rings will be of different sizes depending upon which side of the crystal is nearest the observer.

It is accordingly a primary objective of the present invention to provide means for preventing the above effect, and more particularly, to provide an improved process for growing basal sections of uniaxial crystals wherein the optic axis will be uniformly disposed throughout substantially the entire crystal.

Other objects and advantages will in part appear and in part be pointed out in the course of the following detailed description of one or more embodiments of the invention, which are given as non-limiting examples, in connection with the accompanying drawing in which:

Figure 1 is a diagrammatic view comprising a vertical section through a mold used in the practice of the invention, and

Figure 2 is a diagrammatic sectional view of a crystal grown by means of the apparatus and process illustrated in Fig. 1.

As has already been indicated, a uniaxial crystalline material which is particularly adapted to production by means of the process of the present invention is sodium nitrate, and Fig. 1 illustrates apparatus found useful in carrying out the process to produce a basal section of said material. Container or hollow block 10 in Fig. 1 may comprise any suitable heat-insulating material such, for example, as asbestos or the material sold under the trade name "Marinite." Within container or hollow block 10 there is provided a cavity 12 which may be circular or of any other desired shape. Cup 14 within cavity 12 is illustrated as substantially filled with molten sodium nitrate 15. Cup 14 may be formed from a variety of materials, but preferred results have been obtained with aluminum foil approximately 0.0015–0.003 inch in thickness. Other materials may be used provided however that if the material be one to which sodium nitrate will adhere strictly on solidifying, said material either should have substantially the same cofficient of thermal expansion as solid sodium nitrate or should be readily deformable by the sodium nitrate as the latter cools after crystallization. On the other hand, other rigid materials may be used provided the adhesion thereto of the sodium nitrate is not sufficient to crack or strain the crystal unduly on cooling.

In Fig. 1 it will be noted that an annular space 16 is provided between the outside of cup 14 and the walls. This arrangement is not essential but

is preferred from the standpoint of ease of handling. Element 18 in Fig. 1 represents a cleavage section of mica floating on melt 15 and preferably at least sufficiently smaller in area than cup 14 to fit readily therein. Element 20 in Fig. 1 is a thin plate of rigid material inert with respect to melt 15. Preferred examples of such material include glass and mica, but other materials may be used provided they have melting points sufficiently higher than that of the melt to insure their remaining rigid at the temperatures utilized in the practice of the invention. The improved results obtained by means of the invention appear to derive primarily from use of element 20, as will be explained hereinafter.

In the practice of the invention with the equipment shown in Fig. 1, cup 14 may be filled with ground sodium nitrate and both the hollow block and cup then heated until the charge is completely melted. Preferred results have been obtained by placing both hollow block and cup in a suitable oven such as an electric muffle oven during this step. Alternatively, the sodium nitrate may be melted separately and then poured into cup 14, but in either case it is desirable to heat both the melt and hollow block 10 substantially above the melting point of the charge, as, for example, by the use of an oven heated to an interior temperature of the order of 700–750° F. The next step is to remove the hollow block from the oven, insert plate 20 in the melt and force it to the bottom thereof, and float mica 18 on top of the melt. This operation will be found relatively simple, since mica is not readily wetted by the melt and will therefore float thereon in spite of its greater density. On the other hand, it will readily sink to the bottom thereof if the top is wetted. Care should be taken, however, to prevent trapping air bubbles under either of elements 18 and 20.

The next step of the process is preferably to return the hollow block to the oven for a short heating period, for example 15 minutes, in order to counteract the effects of the cooling while the mica was added and to establish as nearly as possible a uniform temperature throughout the melt. Thereafter the hollow block and melt may be permitted to cool and the rate of cooling should initially be controlled relatively carefully. For example, satisfactory results have been obtained by controlling the cooling to a cycle of from 2–2½ hours to a temperature of the order of 400–450° F. During this cooling period, it is important to insure that the melt cool fastest from the upper surface in order that crystallization may be initiated on mica 18 and in order to prevent the initiation of crystallization elsewhere in the melt. In other words, the thermal gradient in the melt should be maintained from the top to the bottom thereof. It has been found that such control is obtained by following the above procedure, and it may also be desirable to provide the hollow block with an additional cover, such as a sheet 22 of mica or aluminum, to protect the melt from any air currents.

As already indicated, it is preferable to permit the hollow block to remain within the oven until the temperature has fallen to near 400° F., but thereafter it may be removed to conditions of room temperature at any desired time without any appreciable difference in the results. Similarly, cup 14 may be removed from the solidified crystal at any desired point after the hollow block is taken from the oven, as by peeling in the case of the aluminum foil indicated as a preferred material. Mica 18 may be separated from the solidified crystal with comparative ease at room temperature, although it is desirable to aid the separation with a drop of water in order to minimize the danger of stresses producing either cleavage or regions of glide twinning. Plate 20 may be similarly removed at the same time.

When the above steps have been carried out, the product will have substantially the appearance indicated in Fig. 2 and will comprise what may be considered as two different portions. Portion 30 will be by far the larger and will be a single crystal having its optic axis uniformly disposed perpendicular to the surface which was in contact with mica 18 as is indicated by arrow 32. This differs from the results frequently obtained when plate 20 is not used in that in the latter case the optic axis tends to be disposed in the manner indicated by the dotted arrows 33. The other portion 34 in Fig. 2 will comprise what may be termed a species of undergrowth comprising randomly oriented sodium nitrate. The relative thicknesses of portions 30 and 34 will in general reflect the rate of cooling during the period of crystallization. If the thermal gradients in the melt are carefully controlled to produce crystallization only at the surface of mica 18, it is possible to avoid the formation of portion 34 virtually completely. On the other hand, a small amount of this randomly oriented undergrowth is not disadvantageous since if it is of appreciable thickness it will be found to part readily from portion 30 along a well-defined plane 35, and if the undergrowth is thin, it can readily be removed by polishing as, for example, with a belt moistened with water. Thereafter, crystal portion 30 may be ground and polished to any desired final thickness and size.

The process of the present invention is not limited to sodium nitrate nor to the use of mica as the orienting force, although preferred results have been obtained with mica. Other crystals having a surface comprising the desired atomic network may also be used, providing they also are not structurally altered at the fusion temperature of the new crystal and provided they may be detached therefrom without damage to the new crystal. This last essential is particularly aided by flexibility as in the case of mica. It is also preferred, but not essential, that the orienting substance and the crystal have substantially matching coefficients of thermal expansion in the plane of contact therebetween. Examples of other crystals which may be grown by the process of the invention include mixtures of sodium nitrate with, for example, silver nitrate. The above-identified joint application also discloses the use of mica in the growing of large, single crystals of other alkali metal compounds, such as alkali halides. The present invention is equally applicable to said materials but since they are isotropic the problem of convexity, or non-uniform disposition of the optic axis, does not arise.

Since certain changes in carrying out the above process may be made without departing from its scope, it is intended that all matter contained in the above description or shown in the accompanying drawing shall be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all the generic and specific features of the invention herein described, and all statements of the scope of the

invention which, as a matter of language, might be said to fall therebetween.

What is claimed is:

1. In a process of producing a single uniaxial crystal having a predeterminedly oriented axis, the steps comprising forming in an open vessel a melt comprising said crystalline material, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than said crystalline material, bringing into contact with the upper surface of said melt a single crystal of a material substantially infusible at the temperature of said melt, substantially insoluble in said melt, separable from a formed crystal and different than said melt, said second-named crystal having a plane surface thereof in contact with said melt and having said surface extending over at least a greater part of the cross-sectional area of the melt, said surface substantially defining the desired cross-sectional area of the said crystal to be formed, and initiating crystallization of said melt on said crystal surface by cooling the surface of said melt at a faster rate than the remainder thereof.

2. In a process of producing a single uniaxial crystal having a predeterminedly oriented axis, the steps comprising forming in an open vessel a melt comprising said crystalline material, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than said crystalline material, bringing into contact with the upper surface of said melt a single crystal of a material substantially infusible at the temperature of said melt, substantially insoluble in said melt, separable from a formed crystal and different than said melt, said second-named crystal having a plane surface thereof in contact with said melt and having said surface extending over at least a greater part of the cross-sectional area of the melt, said surface substantially defining the desired cross-sectional area of the said crystal to be formed, initiating crystallization of said melt on said crystal surface by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said crystal surface by maintaining a thermal gradient in said melt from the top to the bottom thereof.

3. In a process of producing a single uniaxial crystal having a predeterminedly oriented axis, the steps comprising forming in an open vessel comprising aluminum foil a melt comprising said crystalline material, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than said crystalline material, bringing into contact with the upper surface of said melt a single crystal of a material substantially infusible at the temperature of said melt, substantially insoluble in said melt, separable from a formed crystal and different than said melt, said second-named crystal having a plane surface thereof in contact with said melt and having said surface extending over at least a greater part of the cross-sectional area of the melt, said surface substantially defining the desired cross-sectional area of the said crystal to be formed, initiating crystallization of said melt on said crystal surface by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said crystal surface by maintaining a thermal gradient in said melt from the top to the bottom thereof.

4. In a process of producing a predeterminedly oriented section of a uniaxial crystal comprising sodium nitrate, the steps comprising forming in an open vessel a melt comprising said sodium nitrate, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than said crystalline material, bringing into contact with the upper surface of said melt a single crystal of a material substantially infusible at the temperature of said melt, substantially insoluble in said melt, separable from a formed crystal and different than said melt, said second-named crystal having a plane surface thereof in contact with said melt and having said surface extending over at least a greater part of the cross-sectional area of the melt, said surface substantially defining the desired cross-sectional area of the said crystal to be formed, initiating crystallization of said melt on said crystal surface by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said crystal surface by maintaining a thermal gradient in said melt from the top to the bottom thereof.

5. In a process of producing a single uniaxial crystal having a predeterminedly oriented axis, the steps comprising forming in an open vessel a melt comprising said crystalline material, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than said crystalline material, bringing into contact with the upper surface of said melt a cleavage surface of mica, and initiating crystallization of said melt on said cleavage surface by cooling the surface of said melt at a faster rate than the remainder thereof.

6. In a process of producing a single uniaxial crystal having a predeterminedly oriented axis, the steps comprising forming in an open vessel a melt comprising said crystalline material, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than said crystalline material, bringing into contact with the upper surface of said melt a cleavage surface of mica, initiating crystallization of said melt on said cleavage surface by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said crystal surface by maintaining a thermal gradient in said melt from the top to the bottom thereof.

7. In a process of producing a predeterminedly oriented section of a uniaxial crystal comprising sodium nitrate, the steps comprising forming in an open vessel a melt comprising sodium nitrate, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than sodium nitrate, floating on top of said melt a cleavage section of mica, and initiating crystallization of said melt on said mica by cooling the surface of said melt at a faster rate than the remainder thereof.

8. In a process of producing a predeterminedly oriented section of a uniaxial crystal comprising sodium nitrate, the steps comprising forming in an open vessel a melt comprising sodium nitrate,

positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than sodium nitrate, floating on top of said melt a cleavage section of mica, initiating crystallization of said melt on said mica by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said mica by maintaining a thermal gradient in said melt from the top to the bottom thereof until said melt has entirely crystallized.

9. In a process of producing a predeterminedly oriented section of a uniaxial crystal comprising sodium nitrate, the steps comprising forming in an open vessel a melt comprising sodium nitrate, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than sodium nitrate, said element comprising glass, floating on top of said melt a cleavage section of mica, initiating crystallization of said melt on said mica by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said mica by maintaining a thermal gradient in said melt from the top to the bottom thereof until said melt has entirely crystallized.

10. In a process of producing a predeterminedly oriented section of a uniaxial crystal comprising sodium nitrate, the steps comprising forming in an open vessel a melt comprising sodium nitrate, positioning at the bottom of said melt a relatively thin element comprising a rigid material inert with respect to said melt and having a substantially higher melting point than sodium nitrate, said element comprising mica, floating on top of said melt a cleavage section of mica, initiating crystallization of said melt on said mica by cooling the surface of said melt at a faster rate than the remainder thereof, and continuing crystallization of said melt on said mica by maintaining a thermal gradient in said melt from the top to the bottom thereof until said melt has entirely crystallized.

11. A process of producing a single crystal, having a predeterminedly oriented axis and a relatively large cross-sectional area, from a crystalline material which comprises the steps of forming a melt of said crystalline material, bringing into contact with said melt a single crystal of a material substantially infusible at the temperature of said melt, substantially insoluble in said melt, separable from a formed crystal and different than said melt, said second-named crystal having a plane surface thereof in contact with said melt and having said surface extending over at least a greater part of the cross-sectional area of the melt, said surface substantially defining the desired cross-sectional area of the said crystal to be formed, said crystal surface having an atomic structure capable of drawing out of the melt and holding a monatomic layer of atoms in a predetermined network having the same geometry as, and substantially the same size as, a like atomic network in the final formed crystal, maintaining another portion of said melt opposite from said crystal surface in contact with a rigid element, said rigid element acting to prevent warping of said crystal during cooling, initiating crystallization of said melt on said crystal surface by cooling said melt adjacent said surface at a faster rate than the remainder of said melt, and separating said first-named crystal after formation from said second-named crystal.

CUTLER D. WEST.

Certificate of Correction

Patent No. 2,414,679 January 21, 1947

CUTLER D. WEST

It is hereby certified that errors appear in the printed specification of the above numbered patent requiring correction as follows:

Column 2, line 45, for "cofficient" read *coefficient*; column 6, line 57, for "crystal" read *cleavage*;

and that the said Letters Patent should be read with these corrections therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 4th day of July, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.