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[54] **PROCESS FOR THE CULTURE OF LARGE MONOCRYSTALS OF LITHIUM NIOBATE**
8 Claims, 1 Drawing Fig.

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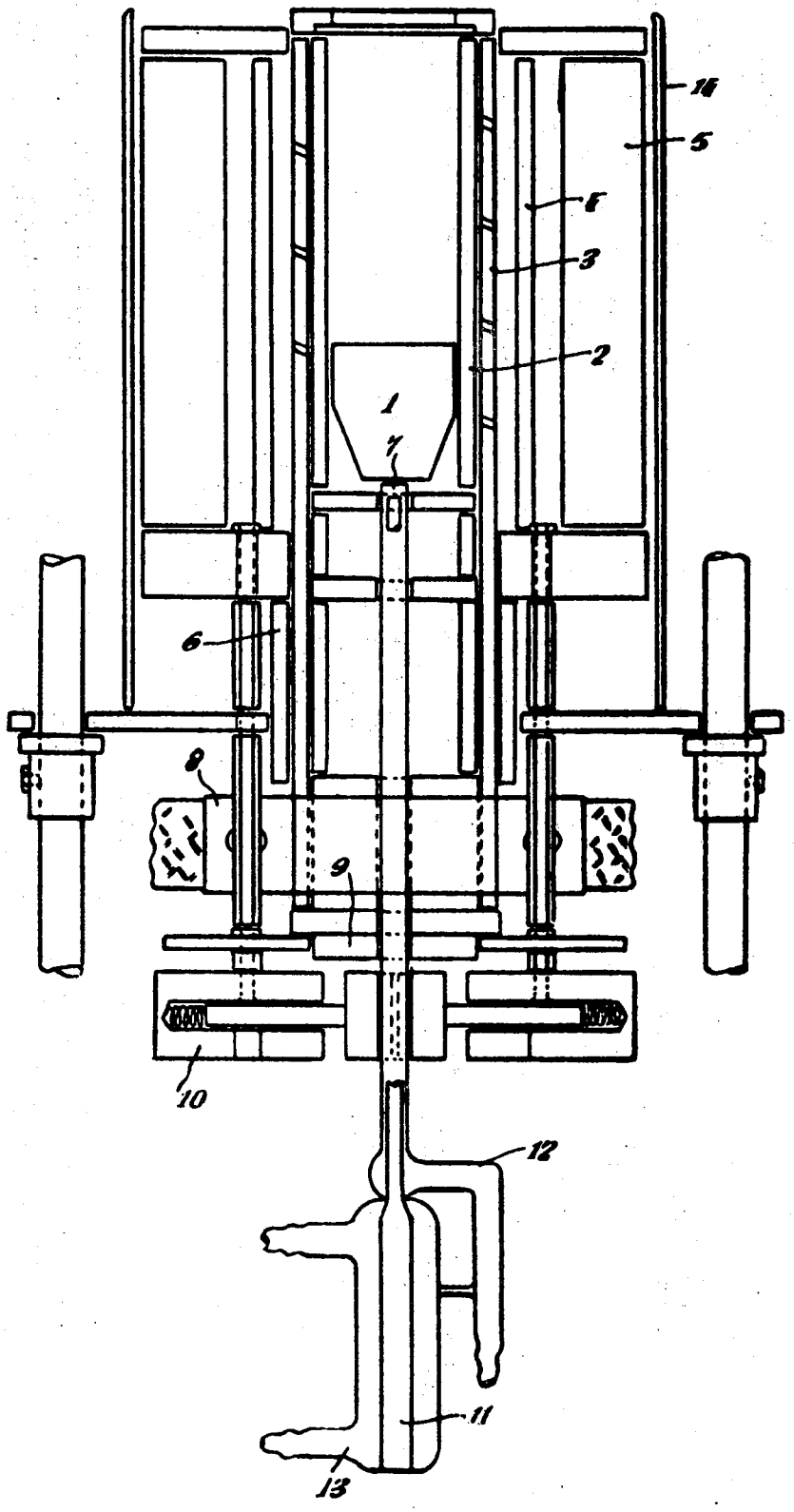
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ABSTRACT: The present invention relates to a process for cultivating larger unstressed single-domain crystals containing niobium and an alkali metal, preferably lithium. The process is conducted by the Zochralski technique for cultivating crystals from a melt in an oxidizing moist atmosphere by means of resistance heating, which maintains an electric short circuit between crystal seed and the melt.


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PROCESS FOR THE CULTURE OF LARGE MONOCRYSTALS OF LITHIUM NIOBATE

Cross-Reference

This application is a continuation in part of application Ser. No. 692,622, filed Dec. 1, 1967, now abandoned.

BACKGROUND OF THE INVENTION

The present invention provides a process for cultivating monocrystals from a melt, which crystals comprise $MeNbO_3$ in which Me represents an alkali metal atom, preferably lithium, or lithium which in some lattice positions are replaced by other alkali metals, and if desired with addition of doping substances, for example, oxides of rare earths, alkaline earth metals or transition elements, the crystals being cultivated in the presence of an oxidizing atmosphere with an increased content of water vapor, preferably in an atmosphere of moist oxygen.

The present invention relates preferably to niobate crystals. Lithium niobate became a center of general interest due to the search for a ferroelectric material that is easy to use as single-domain crystals for electrooptical elements at room temperature. Not only its usefulness as modulator for laser light is now being studied, but also the possibility of directing light for the production of large screen television pictures. Of further great interest is the nonlinear optical behavior in mixing two laser beams and frequency multiplication. The whole matter became especially interesting when it became possible to cultivate monocrystals of this material and to investigate their extremely favorable properties. This explains the great demand for especially large (longer than 20 mm.), optically satisfying single-domain monocrystals.

The process for their culture hitherto known are unsatisfactory for several reasons:

1. As far back as 1958 Reisman and Holtzberg (J. Amer. Ceram. Soc.80, p. 6503) ascertained during the examination of the phase diagram that a $LiNbo_3$ melt readily loses oxygen and turns brown. This reduction can be subsequently reserved by tempering in oxygen at 1100° C, but this does not always get rid of the coloration.

This further oxidation may be carried out simultaneously with the polarization of the crystals in the electric field, the purpose of which is the production of single-domain crystals.

2. When extremely pure starting materials are used, the culture crystals, after having been drawn in air or in air with an additional amount of oxygen, generally crack on cooling so that only fractions of a few millimeters length are left.
3. When single-domain crystals are produced by subsequent tempering in an oxygen atmosphere in an electric field, the crystals crack in the vicinity of the cathode and undergo discoloration. This means a further loss of substance. The largest lumps so far commercially available for scientific purposes that can be cut out in unstressed form after the manufacture, are cubes having sides about 5 mm. long.
4. High-frequency induction heating, which is used almost exclusively, is unsatisfactory because the fall in temperature is not homogeneous:

From the zone where they grow, the crystals far too quickly reach regions of a much lower temperature, after having passed through the ferroelectric conversion temperature. It has therefore already been proposed to use resistance "afterheaters" (K.Nassau et al., J.Phys.Chem.Solids 27, Vol. 6/7 p.989 June 1966).

Furthermore, high frequency generators require elaborate controls to stabilize the crucible temperature. When these are used, a special difficulty that arises is the gradual reduction of the high-frequency output for cooling, after crystal culture.

The present process yields unstressed, relatively very large and colorless single-domain crystals in a single operational step.

The invention is illustrated, by way of example, with reference to the accompanying drawing, the single FIG. of which shows a culture apparatus in vertical section.

The apparatus used is the conventional apparatus according to the Zochralski technique (see, for example, A. Smakula "Einkristalle,"c Springerverlag, Berlin 1962). In contrast to other culture methods, in which high-frequency heating is used, the present process uses resistance heating. The melt, for example, an $LiNbO_3$ melt, is introduced into a platinum crucible **1** which is located in the center of a vertical, MgO ceramic tube **2**, without touching it. A SiC heater element **3**, supplied with current by leads **8**, envelopes the ceramic tube along the whole of its length. The apparatus is also surrounded by radiation shields, **4** and **14**, and heat insulation **5**, **6** and **9**. Temperature measuring is carried out, both for control and checking with Pt-PtRh (10 percent) thermoelements, one of which **7** is located directly underneath the bottom of the crucible. With the control used, the temperature at the thermoelement can be kept constant at about 1250° C.±0.8° C. A reference element **11** is placed in a water-cooled container **13**.

The seed crystals or the crystals formed are semiconductors and above a temperature of about 700° C. are also ion-conductors. The short circuiting of the resistance heating between seed and melt enables polarization charges to flow off as they are formed by the conversion in the ferroelectric phase. The short circuit prevents the formation of an external field, and therewith the necessity of investing additional energy for this field.

A supply of gas **12** from below enables the furnace atmosphere to be chosen at will, so long as it is oxidizing and moist, within certain limits, and it may have an admixture of inert gases. The oxidizing atmosphere is one which contains oxygen either as pure oxygen alone or as a mixture of oxygen and inert gases which is rich in oxygen. Any mixture of gases employed preferably contains at least 50 volume percent and most preferably from 80 to 100 volume percent of oxygen, referring to dry gas. Thus, air enriched with about 50 percent oxygen or higher is a suitable source of an oxidizing atmosphere. Inert gases such as nitrogen, noble gases, nitrogen oxides may be present. Best results are obtained when pure moist oxygen is used for cultivating the crystals. The amount of moistness contained in the oxidizing atmosphere is that amount of moistness which corresponds to a 100 percent steam partial pressure at a temperature of from 22 to 28° C. and preferably, about 24 to 26° C. This constitutes more water vapor than is normally present in the gases employed in art processes and may be provided by supplying water from an external source. Suitably, all of the gases to be employed are passed through a vessel containing water prior to entering the furnace. The rate of gas flow and the temperature of the water are kept at levels which provide the desired amount of water vapor in the total gas. Flow rates of gas corresponding to 0.3 to 3.0 and preferably 0.5 to 1.0 liters per hour through, or over water kept at 22° C. to 28° C. produce best results.

If required or desired, the monocrystal formed is tempered in situ at a temperature below its melting point but of its order of magnitude, either in moist oxygen or in a mixture of moist oxygen and at least one inert gas. The apparatus described is suitable for cultivating reproducibly large, purest $LiNbO_3$ crystals or mixed crystals (in which Me has the meaning defined above) of 15 to 18 mm. diameter and 30 to 50 mm. length, and these crystals have no tendency to crack.

Control experiments

A. Crystals were cultivated in a parallel experiment under identical conditions, except that dry oxygen instead of moist oxygen was used. This, for example, can be done by using oxygen from an oxygen bottle which has been passed a drying tower. As expected, cracks appeared in the monocrystal during cooling; this proves that when extremely pure and stressless, large monocrystals are to be obtained the presence of water vapor in the culture atmosphere is imperative.

B. Another parallel culture experiment was carried out by a known method, using 1 atom percent Mg. in the form of MgO, and then tempering in an oxygen atmosphere. When using this method this is an optimum MgO concentration which reduces stresses, and neither an excess nor a deficient amount with regard to this percentage is permissible. When these crystals were taken out of the culture apparatus, all of them were found to have turned brown and only when they were tempered in oxygen and an electric field was applied did they become water clear. Nevertheless, these crystals cracked, especially in the region near to the cathode.

An investigation of this phenomenon revealed the appearance of an infrared double band at 2900 cm.^{1} in all crystals doped with MgO. It was found that tempering in the electric field, released an electrolytic process which caused an MgO accumulation predominantly in the vicinity of the cathode, while the band could not be detected in the partial regions near to the anode. This produces a colorless crystal structure in the vicinity of the anode, but, at the same time, heterogeneity in the crystal as a whole, and merely shifts the cracking tendency to the region nearer to the cathode.

In comparison with the foregoing, the present process offers the following important advantages, at the same time allowing the crystals to be cultivated in a simpler apparatus:

a. Extreme purity and homogeneity of the monocrystal.

b. Reproducible culture of large (over 40 mm. long) stressless, alkali metal niobate crystals of optically high quality, which possess nearly ideal crystallographic structure comprising few small angle grain boundaries and a low density of dislocations.

c. Etched and ground specimens reveal that the short circuit employed in the cultivation of the crystals drawn in the (001) direction practically consist of a single ferroelectric domain. Regions with differently oriented domains are very small. Tempering following immediately after culture can in many cases be dispensed with.

These advantages are achieved, according to this invention, by the cooperation of a moist oxidizing atmosphere (without a stoichiometrically defined incorporation of H_2O or OH^1 in the crystal lattice), the electric short circuit between crystal seed and crucible (or the melt) and the temperature drop which is easier to regulate in crystal culture by the electric resistance heating provided.

Example of the culture of an $LiNbO_3$ monocrystal

Fusing the starting material: Extremely pure $LiNbO_3$ powder is tamped with a clean plastic pestle into a tared platinum crucible and fused in the culture furnace. During the heating period, a moist current of oxygen is passed through the furnace from below at the rate of 0.5 liter per hour. The oxygen is first moistened by passage through a washing bottle filled with distilled water kept at a constant temperature of 25° C. thus assuring a 100 percent steam atmosphere in the current of oxygen which corresponds to this temperature.

The material collapses extensively during melting and is repeatedly made up again by adding portions of about 2g. each by mans of a long quartz funnel which must not touch the melt.

Adding the dope: For certain purposes, for example, in laser technique, doped monocrystals are desirable. Suitable dopes are, for example, the oxides of rare earths, of the alkaline earth metals or of transition elements. In such a case, the crucible is cooled before the last 2 to 4 g. of the niobate, e.g. $LiNbO_2$, are added, and the resulting cold melt is accurately weighed to ensure the precise ratio of $LiNbO_3$ and the chosen dope. Advantageously oxides of rare earths are used, for example 0.1 to 2.0 atom percent Nd or Pr in the form of Nd_2O_3 or Pr_2O_3.

In the present Example the cold unbroken melt is doped with 0.5 atom percent Nd of finely ground Nd_2O_3. To prevent vaporization losses of the dope during renewed heating, the whole is covered with the remainder of the $LiNbO_3$, which had been taken into account, and fused again.

Temperature regulation

Underneath the crucible, two thermoelements are provided: One is used for checking the temperature by means of a mV-recorder and the other is connected with a temperature governor. The latter thermoelement is located very near the heater element to ensure better temperature constance in the crucible. In this manner, the adjustable variation can be improved from ±4° C. to ±0.8° C. in the crucible. On completion of the melting of the material in the crucible, the initial temperature is set; in most cases it is about 15 to 20° C. above the melting point. The seed oriented by X-ray diffraction (direction of growth, for example, parallel or perpendicular to the *c*-axis) is fixed and centered above the melt in the crystal holder with the aid of platinum wire. The crystal holder is connected electrically with the platinum crucible via crystal culture mechanism and via a lead with the crucible pedestal. If possible, the initial temperature regulation should be so adjusted that the seed retains its size and does not change its diameter while being drawn through its first 2 to 4 mm. of its growth.

Crystal drawing

The crystal is drawn by the Zochralski method as described, inter alia, by Smakula. During the drawing, the temperature must be lowered to maintain the desired constant diameter of the crystal. It has proved advantageous to use a drawing speed of 1 to 2 cm. per hour and a seed turning speed of 0.2 to 1 turn per second.

Tempering and cooling

When the crystal has reached the desired length the crucible is lowered until the crystal detaches itself from the melt. This prevents the crystal from being displaced relatively to the furnace and suffering considerable temperature variations of tremors. The furnace is then covered, the current of moist oxygen increased to 1 liter per hour, the temperature set at about 50–80° C. below the melting point and the crystal is tempered for 12 hours. During 36 hours, the temperature is then lowered to room temperature.

I claim:

1. In a process for cultivating single domain lithium niobate monocrystals from a melt and crystal seed by the Zochralski method, which crystals may be doped by oxides of rate earths, the improvement consisting essentially of heating the melt by means of resistance heating, maintaining an electric short circuit between the crystal seed and the melt and cultivating the monocrystal in a moist oxidizing atmosphere containing at least 50 volume percent of oxygen and having a steam partial pressure which corresponds to saturation at a temperature of from 22 to 28° C.

2. A process according to claim 1, wherein said moist oxidizing atmosphere contains at least 80 volume percent of oxygen.

3. A process according to claim 1, wherein said moist oxidizing atmosphere contains at least 80 volume percent of oxygen and has a steam partial pressure which corresponds to saturation at a temperature of from 24 to 26° C.

4. A process according to claim 1, wherein said oxidizing moist atmosphere has a steam partial pressure which corresponds to saturation at a temperature of from 24 to 26° C.

5. A process according to claim 1, wherein said moist oxidizing atmosphere has a steam partial pressure which corresponds to saturation at a temperature of 25° C.

6. A process according to claim 1, wherein a doping material is included in the melt in an amount of 0.1 to 2.0 atom percent Nd in the form of Nd_2O_3.

7. A process according to claim 1, wherein a doping material is included in the melt in an amount of 0.5 atom percent Nd in the form of Nd_2O_3.

8. A process according to claim 1, wherein the moist atmosphere consists of oxygen and water vapor.